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FLAME PHOTOMETRY OF PHOSPHORUS AND SULFUR BY GRAPHITE ATOMIZER VAPORIZATION

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BY

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This dissertation is dedicated

to my parents.

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ABSTRACT

FLAME PHOTOMETRY OF PHOSPHORUS AND SULFUR
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Because phosphorus is a common pollutant in natural waters, there is a need to develop a convienent, reliable technique to measure low phosphorus concentrations. Spectrophotometric procedures involving the molybdenum blue complex have so far proven to be the best technique for measuring phosphorus in the 0.01 to 10 mg/L range, however, these procedures are all time consuming and subject to interference.

This dissertation deals with flame photometry as a method for phosphorus analysis. In a hydrogen-rich flame phosphorus atoms undergo a chemiluminescent reaction to form an excited HPO molecule, which emits with maximum intensity at 526 nm. Normally this method is used to selectivity detect phosphorus compounds separated by gas chromatography,

or to analyze gas phase phosphorus concentrations. When aqueous solutions are introduced to the flame as aerosols, sensitivity is reduced and metal ions interfere with the emission. An alternative method of sample introduction is evaluated in this dissertation. A Perkin-Elmer HGA 2100 graphite atomizer is coupled to a flame photometer. Samples containing 25 μL of aqueous phosphate solutions are placed in the atomizer with a micropipet. The atomizer dries the sample at 110^{o}C, then vaporizes the phosphorus compound at 2500^{o}C. The phosphorus vapor is swept into the flame and the HPO emission is measured. Intensity is directly proportional to phosphorus concentration. This method of sample introduction has fewer metal ion interferences than the aerosol technique, however, common ions such as calcium, magnesium, and iron III, still interfere. Releasing agents such as EDTA and sodium silicate failed to eliminate the metal ion interferences. It was subsequently demonstrated that the metal ion interference takes place in the vapor phase after atomization.

It was found that silica reduced the degree of interference. A method of permeating the graphite tube with silica was developed. The procedure involves impregnating the graphite tube with $SiCl_4$ under reduced pressure, hydrolyzing $SiCl_4$ to hydrated silica, drying and firing at

a high temperature. The high temperature firing causes the dried silica to react with the graphite forming silicon carbide. This was confirmed by weighing tubes before and after treatment with silica and after firing.

The appearance temperature for phosphorus as phosphate in the presence of calcium is 1400°C for untreated graphite and 2000°C for the silicon carbide coated tube. At the higher temperature, the metal-phosphorus interaction causing the interference is less favorable, thus causing a reduction in the extent of the interference.

Eleven possible interfering ions were tested to determine the degree of interference on a 1 mg/L phosphorus solution. Among the 11 ions tested, none of them had a signal depressed more than about 10%, when the ion concentration was at 10 mg/L. When tested at the 100 mg/L ion level, six of the ions caused a deviation of more than 10% from the signal which a 1 mg/L phosphorus solution would give.

The relative standard deviation for five, 25 µL samples of phosphorus is 3 to 6% at a concentration of 1 mg/L. The detection limit is 0.04 mg/L for a 25 µL phosphorus solution.

By making a few minor modifications to the instrument, sulfur can be determined. Sulfur is also subject to metal ion interferences but this element was not studied as extensively as phosphorus.

I. INTRODUCTION

Phosphorus

Probably more than 95% of the phosphorus content of igneous rocks occurs as apatites, $CaX_2 \cdot 3Ca_3(PO_4)_2$ where X could be fluoride, chloride, or hydroxide ion. The most common is fluoroapatite, $CaF_2(PO_4)_2$. The leaching action of water and lichen on igneous rocks causes the phosphate minerals to dissolve from the rock. Because natural phosphate minerals are very insoluble, the total phosphorus concentration in natural waters seldom exceeds 1 mg/L. The concentration of phosphate ion, which is the form that can be directly absorbed by plants, is quite a bit less. In ocean water phosphorus occurs at a concentration of 30 mg/L in the upper levels where there is enough light for the growth of algae. At lower levels, phosphorus concentration normally increases to about 150 μg/L. Plant life contains 1-3% phosphorus, which is tied up in organic compounds such as nucleic acids, and intermediates used for protein synthesis and carbohydrate metabolism. Because plants need a lot of phosphorus, and the concentrations of phosphorus in natural waters are very small, phosphorus often limits the rate of plant growth. Muncipal sewage

contains anywhere frcm 1 to 25 mg/L phosphorus, of which about 30-70% is polyphosphate from detergents (1). When this enters rivers or lakes it causes blue-green algae to grow rapidly with an associated increase in bacterial decay. These processes soon deplete the supply of oxygen which causes eutrophication in natural waters.

From this brief discussion, one can understand the need for quick, reliable methods of phosphorus analysis. Although many methods are available there are still problems involved with analyzing the various forms of phosphorus that occur in water. Even the determination of orthophosphate itself can be a problem. Some of these problems will be explained in the following sections.

Separation and Conversion of Different Phosphorus Forms to Orthophosphate

Phosphorus containing substances are generally analyzed as phosphate. This is probably because phosphate is the most stable form of phosphorus. Almost any dissolution process used, will convert phosphorus to this form.

Phosphate rock readily dissolves in a strong acid solution. Any residue is fused with sodium carbonate, then is combined with the orginal so that it can be analyzed (1).

In the case of organophosphorus compounds the Schöniger oxygen flask method can be used. Here a sample is ignited and quickly inserted into the flask containing pure oxygen

and an absorbing solution. When combustion is complete, the solution is removed and analyzed for phosphorus (2).

Samples such as foods and fertilizer are put into a Kjeldahl flask and acids are added to oxidize easily oxidizable material. After the flask has cooled, perchloric acid is added; then it is heated until the oxidation is complete (3).

In all of these methods there are many interfering elements. Many of these elements can be removed during the sample dissolution process. In many cases the interfering substances are removed after dissolution, by means of one of the classical techniques of separation such as, electrodeposition, ion exchange, thin layer chromatography, liquid-liquid extraction or precipitation of phosphate complexes such as magnesium ammonium phosphate or ammonium molybdophosphate. However, during the dissolution and separation procedures, there is always the possibility of sample loss or contamination. Therefore, these methods work well when the phosphorus concentration is 0.1% or higher, but when it is in the part per million or part per billion range, as in many water samples, then other methods of sample preparation should be utilized.

Phosphorus compounds that exist in water are classified as inorganic, organic, and polyphosphates. The problem is to convert all of these forms to orthophosphate, which is then usually determined spectrophotometrically. It is

rather difficult to identify each individual type of phosphorus compound in a water sample. In practice several classifications of phosphorus concentrations are established on an operational basis. Filterable phosphorus is the portion of the sample that passes through a 0.45 μm membrane filter. The nonfilterable fraction is the portion that is retained by the filter and usually represents a majority of the particulate phosphorus. The filter size is arbitrarily selected to provide a basis for comparing phosphorus determinations and is a compromise between a filter with pores small enough to collect as much particulate material as possible, and yet has large enough pores to permit a rapid separation. One uses the terms "filterable" and "nonfilterable" instead of "soluble" and "particulate" phosphorus because not all of the particulate matter may be collected.

Both filterable and nonfilterable fractions are further divided into orthophosphate, acid-hydrolyzable, and organic phosphate.

Orthophosphate is the form of phosphorus that will react directly with a color reagent, so that it can be readily determined directly by an optical absorption method.

Acid-hydrolyzable phosphorus is phosphorus occurring in a compound that will be converted to orthophosphate by acid hydrolysis.

Organic phosphate is usually determined by one of three digestion methods (4). The perchloric acid method is the strongest oxidizing and most time consuming method. It is recommended only for difficult-to-oxidize samples such as sediments. The nitric acid-sulfuric acid method is recommended for most samples. The easiest method is the persulfate method. But the results for a given type of sample should be compared to those from a stronger digestion method to make sure that all of the organophosphorus compounds are digested.

Goosen and Kloosterboer (5) developed a method for digesting a water sample by the use of UV light. The combined effect of both UV light and heat from the lamp converts both acid-hydrolyzable and organic phosphate to orthophosphate. If a thin aluminum screen is placed between the lamp and the acidified sample, only hydrolysis occurs.

Various phosphorus forms can be classified into six categories. In addition to these, there are six possible combinations of analysis that can be reported as total phosphorus concentration.

Three of the total phosphorus determinations arise from orthophosphate, acid-hydrolyzable, and organic phosphate digestions performed on the sample; but each of the analyses performed on these three fractions could include filterable and nonfilterable phosphorus as well.

Two of the total phosphorus determinations would come from digesting the sample for total filterable and total nonfilterable phosphorus.

The summation of the phosphorus concentrations from the three chemical types and the filterable and nonfilterable fractions gives the total concentration of phosphorus in the entire sample.

Most instrumental methods will measure only orthophosphate and not be able to distinguish the various chemical forms of phosphorus. Therefore, in order to report the total phosphorus concentration, one must digest all forms of phosphorus to the orthophosphate form prior to the analysis.

Nonchemiluminescent Methods of Analysis

Although many techniques are available, spectrophotometric methods are the most widely used for trace phosphorus determination in water (1). Most spectrophotometric methods based on some variation of formation of a molybdenum complex. Rather than describing any one method in detail, it would be more useful to describe some of the complexes in general.

If an excess of molybdate solution is added to an acidic solution of orthophosphate, a yellow color is produced. The color is due to the formation of molybdophosphoric acid, $H_3PMo_{12}O_{40}$ which will form

from no phosphorus compound other than orthophosphate. The concentration of this complex can be determined spectrophotometrically at about 400 nm. Its molar absorptivity is 1300 L/mol cm.

For this method of analysis the optimum concentration range is 2 to 25 mg/L of phosphorus, which means it has limited use for water analysis. It is also subject to the following interfering ions: silicate, arsenate, tungstate, vanadate, bismuth, nickel II, copper II, and fluoride. It is possible to increase sensitivity and reduce some of the interferences by extracting the sample into an organic solvent.

Reducing the molybdophosphoric acid complex with a reductant such as hydrazine sulfate or chlorostannous acid will give a heteropoly blue complex. If at the time of reduction, the acidity is about 1.0 N in sulfuric or perchloric acids the maximum absorbance is between 820 to 830 nm, and the complex formed is known as a "heteropoly blue" complex. This has a molar absorptivity of 26,800 L/mol cm, which gives an optimum working range of 0.1-0.2 mg/L of phosphorus.

At lower acidities the blue compound formed is called the "molybdenum blue" complex. Its maximum absorbance range is 650 to 700 nm with a molar absorptivity of 18,000 L/mol cm. Either of these complexes can be used for spectrophotometric work. However, care should be taken in

controlling the acidity, the choice of reductant, the reaction temperature, and the time allowed for the reduction to take place.

The following ions interfere and must be absent: tin II, nitrate, arsenate, iron III, and tungstate. Cations that form a precipitate with sulfuric acid must also be absent.

Instead of reducing the molybdophosphoric acid complex in aqueous solution, one can carry out an extraction with the reducing agent in the organic phase, reducing the complex to the heteropoly blue (6). This reduces the extent of several interferences but does not improve sensitivity. McKay (7) was able to obtain a detection limit of 0.001 mg/L of phosphorus, using an extraction procedure. If a molybdate solution is added to an acidified solution containing orthophosphate and vanadate ions, a mixed heteropoly acid is formed. The molar absorptivity is only about 720 L/mol cm at 460 nm, so the optimum concentration range is 5 to 40 mg/L of phosphorus. The advantage of this method is that it is less subject to interference. This method has been modified to give a molar absorptivity of 25,400 L/mol cm, which puts the optimum working range between 0.1 and 1.2 mg/L of phosphorus at a wavelength of 310 nm. One can also use an extraction procedure with the molybdovanadophosphoric acid complex. It has about the same spectrophotometric characteristics as the procedure just

explained.

From this brief summary of the spectrophotometric methods that are available, one can appreciate the limitations and how much care is required in working with these methods. One can also recognize the many pitfalls and should realize the lack of complete understanding of the chemistry taking place. For these reasons other methods are more desirable, especially ones that can readily solve sample preparation and analysis problems.

There are a number of gravimetric and titrimetric methods available (1,8), most of which involve the formation of an ammonium moybdate complex with phosphorus. These methods have the disadvantage of being time consuming, especially in the case of the gravimetric analysis.

Neutron activation analysis has been used for phosphorus determination, using the beta emission from ^{32}P. However this method is quite expensive and as a result it is not very widely used (9).

X-ray fluorescence has been used to measure the phosphorus concentration in textiles, in which phosphorus additives are used to make flame retardant clothing. However, because of the low atomic number of phosphorus, the x-ray yield is low and the sensitivity is limited.

Leyden et al (11) determined the concentration of phosphate in natural waters using x-ray fluorescence spectrometry. The phosphate is complexed as

12-molybdophosphoric acid which is then extracted. This removes germanium, silicon, and arsenic compounds that can cause interferences. The 12-molybdophosphoric acid is then adbsorbed onto silica gel, enabling the molybdenum x-ray yield to be measured. This technique shows increased sensitivity for two reasons. First, there are twelve molybdenum atoms for each phosphorus atom; second, the x-ray yield for molybdenum is much higher than that for phosphorus.

Emission spectrometry has often been used to analyze phosphorus in lubricating oils in the 0.02-0.2% range (12).

Fassel and Knisely (13) were able to measure as little as 0.04 mg/L of phosphorus with an emission spectrometer that utilized an inductively coupled plasma as its source.

Flame emission spectrometry can be used with a hydrogen-air flame to detect as low as 5 mg/L phosphorus when the phosphorus monoxide band is used at 246.4 nm (14).

In most flame emission techniques an indirect method is used. The instrument is set to observe an atomic line for an element such as calcium. Then the amount of phosphorus in a solution spiked with an excess of calcium ion is related to how much the phosphate attenuates the calcium signal (15,16). Atomic absorption performed directly is often too insensitive, because the more intense resonance lines are in the UV where flame gases absorb (17,18). Indirect methods using molybdenum complexes have been used

with atomic absorption where the molybdenum metal is analyzed. The optimum concentration range is 0.1-1.2 mg/L phosphorus. This method may appear to have advantages over the spectrophotometric methods, but it is still subject to many of the same interferences (19,20,21,22).

Crawford, Lin and Huber (23) developed the use of atomic absorption spectrophotometric inhibition titration for the determination of phosphates and polyphosphates in surface and wastewaters. In this method a standardized magnesium ion solution is titrated automatically into the phosphorus sample at a constant flow rate. Simultaneously the sample solution is aspirated into the flame of an AA, whose wavelength is set at the magnesium resonance line. The equivalence point is observed when there is an increase in absorption from excess magnesium ion. The stoichiometry is not always predictable because it depends on the flame conditions and the type of phosphorus compound. For this reason known phosphorus compounds must be determined prior to the analysis of the unknown. This technique was used to determine phosphate and polyphosphate simultaneously, and Lin and Huber (24) used it to determine phosphate, sulfate, and silicate simultaneously in one titration. A disadvantage is that one must put the sample through a cation exchange resin, which is in the hydrogen form, prior to the analysis in order to remove all metal ions.

A cathodic stripping chronopotentiometric method (25) has been developed in which a copper II phosphate salt film is stripped from a copper electrode. The detection limit for phosphorus is 10 μg/L.

Huber et al (26) studied the cathodic response characteristics of a lead oxide electrode for polyphosphates in the presence of orthophosphate.

Tanaka et al (27) used a lead ion selective electrode to determine phosphate. The electrode responds to a concentration of $1X10^{-5}$ M to $1X10^{-1}$ M phosphate with a sensitivity of -19 millivolts per decade of concentration. Arsenate and iodide are the only interferences.

Guilbault (28) used a biologically specific electrode to determine phosphate in water. The electrode consists of two enzymes, alkaline phosphatase and glucose, both immobilized and mounted on a platinum electrode.

Gas chromatography is used when one needs to analyze volatile organophosphorus compounds. Two types of detectors can be used. One utilizes a flame ionization detector treated with alkali salts such as potassium, rubidium, and cesium sulfate in the vicinity of the flame (29). This gives an enhancement for organophosphorus compounds by about a factor of a thousand.

The other type detector is a flame photometric detector. This is the type used in the instrument described in this dissertation, and is discussed in more detail in the

next section.

Phosphorus Detection Using Chemiluminescence

Phosphorus can be determined by the use of flame emission, utilizing an excited molecular specie in a hydrogen-air diffusion flame. The emission is a green color and is observed only in a relatively cool flame. The emission has been recorded at a flame temperature of 350°C (17). It was first reported by Salet (30) and later by Geuter (31). Ludlum (32) and Rumph (33) measured the emission bands that occur at 510, 526, and 560 nm. The most intense band is at 526 nm. In 1964, Lam Thanh and Peyron (34) showed that the light emitting compound was the HPO molecule, which is believed to be formed by the following mechanism.

$$P_2 + O \longrightarrow P + PO \qquad 1$$

$$P + OH \longrightarrow PO + H \qquad 2$$

$$H + PO + M \longrightarrow HPO^* + M \qquad 3$$

A number of workers (18,35,36,37) have noticed that the emission can be enhanced by nitrogen or a cooled surface. This enhancement by an inert substance or "third body" has been explained in two ways. One theory suggests that a

third body "M" can be used to remove some of the dissociation energy from the PO species just formed, therefore allowing it to become stable. Gilbert (38) has proposed a second theory that the cooling effect of an inert gas on the wall of a container causes a decrease in molecular motion. H and OH radicals that are required in reactions 2 and 3 then combine at a slower rate. Since these radicals take longer to combine, then they probably reach the end of the flame before the reactions are completed (18).

Sample Introduction Techniques

The flame method works well for gaseous-type samples. In fact it is used as a GC detector, and some workers (39) have obtained a detection limit of 0.0063 mg/L of phosphorus. However, solution samples must be vaporized before any chemical excitation takes place because the flame is too cool to cause this vaporization. If more air is admitted into the flame to raise the flame temperature, then the emission sensitivity decreases. A number of workers have tried various techniques to convert the solution to a vapor.

Dagnall et al (17) introduced the sample as an aerosol and obtained a detection limit of 0.1 mg/L.

Aldous et al (35) passed sample aerosol through an oven to vaporize excess solvent before the sample entered the flame. They obtained a phosphorus detection limit of 0.007 mg/L.

Prager and Seitz (36) used an ultrasonic nebulizer, but obtained a relatively low sensitivity compared to that of air samples. The response was linear from 0.003 mg/L to 0.120 mg/L of phosphorus.

Everett et al (40) vaporized samples on a carbon filament by passing a current through the filament. The vapor then entered the flame, giving a detection limit of 4 mg/L of phosphorus. The authors pointed out that this limit could have been lowered if they had used an optical filter instead of a monochromator.

Belcher et al (41) developed a method called molecular emission cavity analysis (MECA). A sample is placed in a stainless steel cavity, which is then lowered into the flame, and a chemiluminescent emission takes place. Even though no detection limit was mentioned, it was reported that nanogram quantities of sample could be analyzed.

The above methods work well for phosphate solutions, in the absence of heavy metal ions but many workers (17,18,35,40) have found that the presence of metal ions such as calcium, iron III, and sodium causes a large decrease in signal. When metal ions are present, an involatile phosphate is formed that cannot be vaporized by

the relatively cool flame. It is possible to remove metal ions with a cation exchange resin in the hydrogen form.

Although metals have been removed by ion exchange, it is also possible to add a reagent to bind the metal ions. This prevents them from combining with the phosphate, therefore getting rid of the interference problems. The substance used is known as a "releasing agent". Apparently this idea has not worked in the sample introduction techniques mentioned above. Organic solvents have also been found to quench the HPO emission, which would exclude the possibility of a prior extraction of phosphate into an organic solvent (40).

In the work by Campbell and Seitz (42), a commercial graphite atomizer used for atomic absorption was modified and coupled to a flame photometer. The purpose of the atomizer was to dry the sample, then decompose the phosphate salt. The phosphorus present would then be volatilized and carried into the flame photometer by a flow of nitrogen. This worked well for phosphoric acid and its sodium salts, but when metals such as calcium and iron were present, the phosphorus signal decreased. It is believed that these metals formed a metal phosphate that was difficult to decompose into a volatile phosphorus compound. In an attempt to eliminate this interference, EDTA was added to the sample before being placed in the atomizer. It was thought that the EDTA would complex with the metal ion

preventing it from combining with the phosphate ion. This procedure worked, but it was still not an adequate solution to the problem as shown in section III.

The chief objective of the research reported in this dissertation was to develop an adequate method to eliminate this interference problem. It is an important goal of the research to obtain a method of phosphorus determination that remains as simple as possible, so that it can compete with the methods discussed earlier in terms of cost per sample and the length of time for analysis. Therefore, every modification made to eliminate interferences, either in the sample preparation or the instrument, must be kept as simple and as inexpensive as possible. Section III explains the major steps taken, in an attempt to work out an interference-free system.

Sulfur

Like phosphorus, sulfur is also widely dispersed throughout the earth's crust. Large masses occur underground as elemental sulfur in two areas. Many minerals occur as sulfates or sulfides. Many metal sulfides are extremely insoluble although some sulfides like pyrites will eventually oxidize to sulfuric acid. In plant and animal tissue there are certain amino acids that contain sulfur, one being in the thiol form the other in the disulfide form. Sulfur is required for plant life and is also very useful

industrially. At the same time it can be harmful to man. When sulfur compounds are in a reducing environment, such as sewage, bacteria can reduce sulfate to hydrogen sulfide. Hydrogen sulfide is a weak acid but is poisonous even in relatively small concentrations. Hydrogen sulfide is also found in groundwater and in water from hot springs in relatively large concentrations. Essentially all of the sulfur found in natural waters or wastewaters occurs as either sulfate or sulfide. Therefore, conventional techniques for determining these two compounds in water will be discussed in detail.

Separation and Conversion of Different Sulfur Forms to Sulfate or Sulfide

This section briefly discusses various methods that are used to break down a solid or liquid matrix and to determine the total amount of sulfur present as sulfate or sulfide.

The combustion tube that is ordinarily used for CHN analysis has been modified to do sulfur analysis on organic compounds. A widely used variation is the Pregl method (43). There are a number of closed flask methods. One that has been widely used is the Schöniger flask (2). The procedure used for sulfur analysis is very close to that for phosphorus analysis, so that further discussion here is unnecessary.

Karchmer (44) reports various mixtures of acids that can be used in the wet digestion of metal alloys. A common method for determining total sulfur in inorganic substances such as minerals and alloys is gas evolution. This procedure will work only on substances that are soluble in hydrochloric acid and that liberate hydrogen sulfide. Even so it is commonly used in the steel industry, and there are standardized methods and apparatus available (45).

Nonchemiluminescent Methods of Analysis

Most of the methods of sulfate determination are based on the fact that sulfate ions form an insoluble salt with barium ions.

Probably the oldest and most widely used method is the gravimetric procedure (46). When used for potable water analysis, the other ions present are not in high enough concentration to cause interferences. However, when the ionic concentration is high enough, both positive and negative interferences can arise (47).

A number of precipitation titrations have been developed using heavy metal ions as a titrant. Barium ion is the most widely used. These titrations have the advantage of speed and possibly fewer interferences as compared to gravimetric procedures (48).

Like the titrimetric method, the turbidimetric method is good for low concentrations of sulfate, i.e., below 10 mg/L, while the gravimetric method is restricted to concentrations over 10 mg/L. Concentrations as low as 0.01 mg/L sulfate have been determined using this method (49). A sulfate containing sample is dissolved and precipitated in such a way as to give crystals all the same size. The suspension is then placed in a colorimeter where the light transmitted is measured, or into a nephelometer where the scattered light is measured. Care must be taken to obtain reasonable precision because there are a number of factors that influence the size distribution of the precipitate. This in turn will affect the amount of light scattered. Suspended matter and a colored solution can cause interference, although both of these could be corrected for by filtering and running a blank. Too much dissolved organic matter will affect the precipitation process.

The methylthymol blue method (47) is a colorimetric method of analysis, which is used in autoanalyzers. An excess of barium chloride is added to an acidified sulfate solution to precipitate all of the sulfate. The pH is raised, and a known excess of methylthymol blue is added, forming a blue complex with the excess barium ion. The excess methylthymol blue is gray in color and is measured at 460 nm. Many cations such as aluminum and calcium interfere, so prior removal with a cation exchange column is

suggested.

For sulfide determinations, it must be remembered that there are several possible sulfur compounds contained in a water sample. In most cases one is more interested in the total sulfide, since in the environment the other forms are easily convertible from one form to another depending on pH and the metal ion concentration. However, reference (47) discusses a method of separation and definition of each fraction.

There are generally two methods of sulfide determinations used for water analysis, volumetric and spectrophotometric. The iodometric procedures are the most widely used for sulfide determinations. There is some variation in these procedures, but for the most part they all involve the oxidation of sulfide to either sulfur or sulfate using iodate. A known amount of potassium iodate is mixed with the sulfide sample, which oxidizes the sulfide to sulfate, causing the iodate to be reduced to iodide. One then acidifies the solution to liberate iodine from the unreacted iodate, which is titrated with a standardized thiosulfate solution (50).

The most generally used colorimetric method is the methylene blue procedure (51). The sulfide sample must be acidified to form hydrogen sulfide, which is then added to an acidified solution of p-aminodimethylaniline, in the presence of ferric ion. A reaction takes place forming

methylene blue. A spectrophotometer is used to measure the absorbance at 667 nm. A disadvantage of this system is that the reaction is not quantitative. But the percent yield is fairly constant so this can be used as an analytical method.

Recently other instrumental methods for sulfate and sulfide determination have become more popular mainly because of the decreased time needed for an analysis.

Siemer, Woodriff, and Robinson (52) determined sulfate in natural waters indirectly by the use of electrothermal atomization atomic absorption. Sulfate is precipitated with a known excess of lead nitrate solution, and the excess lead ion is measured in the atomizer using the 405.7 nm lead line. For most samples, the results agreed within 10% of the results from the gravimetric and turbidimetric methods.

Galle and Hathaway (53) used a similiar method for natural alkaline earth water samples. They precipitated the sulfate with barium ion and then measured the excess barium ion at the 553.5 nm barium line using flame atomic absorption.

Yoshida and Takahishi (54) were able to measure micrograms and submicrogram quantities of sulfide in lake and river water. A known excess of mercuric ion was added to the water sample containing sulfide ion. The excess mercuric ion was reduced to mercury vapor which was measured using cold vapor atomic absorption.

Magyar and Kauffmann (55) used x-ray fluorescence for the determination of sulfate in water. Sulfate ion is quantitatively coprecipitated from an excess barium chloride solution. The sulfate concentration in the precipitate is then determined using the x-rays emitted from the barium ion.

Luther and Meyerson (56) used polarography to measure the concentration of sulfate in sea water indirectly. A known excess of lead nitrate solution was added to the sample and the excess lead ion was determined polarographically.

Many ion selective electrodes have been developed for the sulfide ion. Electrodes can generally be used for either direct potentiometric measurements or for locating the equivalence point on a titration.

Weiss (57) utilized a sulfide electrode in both modes and was able to determine sulfide concentration in the 0.003 to 300 mg/L range.

Barica (58) used a sulfide electrode to detect the equivalence point in a titration where a standardized silver nitrate solution is the titrant. The concentration agreed within 3% of the values obtained by the conventional iodometric titration.

Sulfur Determination Using Chemiluminescence

An emission for sulfur, which is similiar in nature to that of phosphorus, was first observed by Salet (30) over a hundred years ago. When sulfur compounds are introduced into a hydrogen rich flame, a blue sulfur emission is observed. This emission is enhanced if a cold object is inserted into the flame.

Fowler and Vaidya (59) made photographs of a sulfur emission spectrum using a flame burning carbon disulfide. They also attributed the bands of the spectrum to the S_2^* molecule. More recently, (60) the S_2^* spectrum has been recorded using newer methods. The most useful portion of the spectrum lies between 320 and 420 nm, where there are approximately 18 bands. Five of the more intense bands are located at 374.1,384.0,394.1,394.7, and at 404.7 nm, with the 384.0 nm band being the most intense.

Sugden and Demerdache (61), orginally proposed a mechanism for the S_2 excitation mechanism, but more recently other workers (62,63), have gained a better understanding of the mechanism. Presently the mechanism is believed to occur as shown below.

$$\text{Sulfur Compound} + \text{Heat} \longrightarrow H_2S$$

$$H_2S + H \longrightarrow HS + H_2$$

$$HS + H \longrightarrow S + H_2$$

$$S + S + M \longrightarrow S_2^* + M$$

$$S_2^* \longrightarrow S_2 + h\nu$$

Both workers agree that the reaction involving the third body "M", is a third order reaction and Sugiyama et al (63), believe it is also the rate determining step. A number of workers have shown that a cold surface in the flame enhances the emission (30,60,64). Dagnall et al (60), does not believe the cool surface behaves as a third body, but he does believe that the third body prevents dissociation of the S_2 molecule. However, after considering the more recent work that has been done on the mechanism, it appears to be possible that the cool surface may act as a third body, possibly in addition to the effect mentioned by Dagnall et al (60). If the reaction involving the third body is the rate determining step, then a cool object inserted into the flame could control the rate of emission.

Below 10 mg/mL of sulfur, Veillon and Park (64) have observed the S_2^* emission intensity to vary as the square of the sulfur concentration. The following equation demonstrates this relationship:

$$I = KC^x$$

where I is the emission intensity x is some power of the concentration C, of the emitting specie, and K is a constant. Taking the log of both sides of the equation gives

$$\log I = \log K + x\log C$$

If one plots the log of the emission intensity versus the log of the sulfur concentation then a linear curve is obtained with a slope of 2. At sulfur concentrations greater than 10 mg/mL, a change in slope occurs, which indicates that the S_2 formation mechanism changes.

Sugiyama et al (63) showed by the use of three-dimensional plots how the flow rates of hydrogen and air affected the value for x.

Eckardt et al (65) not only showed this dependence of x on flow rates, but also showed that x varied according to the type of sulfur compound injected into the flame.

For example, for a given set of flow rates a plot of the calibration curves for sulfur dioxide and methyl mercaptan both showed a nonlinear photomultiplier response. The value for x for sulfur dioxide was 1.95 and for methyl mercaptan, x was 1.71. Erkardt et al (65) also employed a variable exponential function device in conjunction with their detector. For a given set of flow rates and a particular compound, this circuit enabled them to set the

desired value of x to yield a linear calibration curve.

Veillon and Park (64) noticed a 4 to 30 fold decrease in emission intensity with the use of organic solvents replacing the aqueous sulfur solution. This decrease in emission may be due to an increase in flame temperature, but it is more likely to be caused by the organic free radicals formed in the flame from the solvents. These free radicals are known to quench a chemiluminescent emission. If acetylene is mixed with the hydrogen, the sulfur emission is quenched. No emission is observed for compounds containing sulfur as compounds such as $\diagdown\!\!\diagup C{=}S$ or $-\overset{|}{\underset{|}{C}}-SH$ because of the stability of the carbon-sulfur bond. These species are also found to be stable fragments in a mass spectrometer (18).

Other workers, (66,67,68,69), have also studied the effect of organic compounds on the chemiluminescent emission. Sugiyama (66) explains how the organic compound affects the emission mechanism. In general, Farwell and Rasmussen (67) review many of the problems associated with the flame photometric detector that have already been discussed here.

Sample Introduction Techniques

As in the case of phosphorus it is easy to use this chemiluminescent sulfur phenomena for doing quantitative sulfur determinations on gaseous type samples.

Crider (70) has developed an air pollution type monitor using this technique, which is capable of measuring very small concentrations of sulfur dioxide, in the part per billion range.

Gas chromatography detectors have also been constructed (71) using this technique. These prove to be very useful as specific detectors for phosphorus and sulfur-containing compounds. Bowman and Beroza (72) used a dual phosphorus-sulfur detector arrangement with which they can identify pesticides by measuring the phosphorus to sulfur ratio characteristic of each pesticide molecule. These detectors can generally detect phosphorus compounds at the part per trillion level and sulfur compounds at the part per billion level.

In solution type samples one must use an aerosol. However, the presence of most cations will cause an interference, generally resulting in a decreased signal. This problem has been recognized by many workers (18,60,73). So far the best solution to the problem is the prior removal of all cations by using a cation exchange resin in the hydrogen form. This will convert any sulfate salts to sulfuric acid, which shows no interference.

Often, using an ion exchange resin in an analysis is impractical because of the possible sample loss, and increased analysis time. Therefore the objective is to develop a sample introduction technique that will remove

potential metal ion interferences before being introduced into the chemiluminescent emission. This method involves putting a known volume of sample into a graphite atomizer, drying the sample, then volatilizing it at a higher temperature to allow the vapor of the sulfur species to enter the flame emission. The procedure described above can be carried out very easily; unfortunately, some metals present in the sulfur sample will cause an interference. Neither time nor facilities permitted an in depth study of the reactions in the atomizer that were causing the interference. Instead, some simple experiments were performed giving information on how sulfur behaved in the atomizer. Also experiments to demonstrate the method's analytical potential were conducted.

An important part of the research was to also establish the extent of interference for a number of metal ions at various concentration levels.

Electrothermal Atomization

There are a number of reasons that graphite atomizers are replacing the flame cell in atomic absorption. For one, the atomizer gives the instrument 2 to 3 orders of magnitude greater sensitivity. This results in detection limits much lower than those obtainable by flames.

A second advantage is that many samples can be placed in the atomizer without a prior digestion step. Even solids and liquids can be analyzed. Small samples can be analyzed more readily using an atomizer, which makes it useful when large samples are difficult to obtain, such as in clinical or forensic applications. However, small samples can be a problem where the substance being analyzed is heterogenous in nature (74).

A graphite atomizer is designed to be inserted in place of the burner in an atomic absorption instrument. Thus the function of the graphite atomizer is the same as that of the flame, i.e. to transform the element to be determined into an atomic vapor.

Graphite atomizers are constructed as a resistance type furnace that typically operates between room temperature and 3000°C. The heating operation is usually carried out in either two or three steps. The temperature and the time required for each step are adjusted according to the type of sample being analyzed. Generally, anywhere from 10 to 100 μL of sample is inserted into the atomizer, then the sample is dried, usually at 110°C. Typical drying times are 10 seconds for every 10 μL of sample solution. If there is organic matter either dissolved or suspended in the sample, then the second heating cycle or charring step decomposes this organic matter present. This step is not included if there is no organic matter present. Next, in the

atomization step the sample is vaporized and reduction occurs. A certain fraction of the light from the hollow cathode lamp is absorbed by the atoms in the atomizer. Depending on the element determined, the atomization temperature will generally be somewhere between 1200 to 2700^{o}C and the time set between 3 to 10 seconds. The absorbance is usually readout as peak height. However, in some cases the sample matrix can prevent the element from being reduced immediately. In these cases the absorbance is measured by measuring the peak area. While the heating cycles take place, nitrogen is allowed to flow through the atomizer. The nitrogen flow sweeps out moisture during the drying stage and also sweeps out the residual sample leftover from the previous atomization step. The nitrogen flow also excludes oxygen from the atomizer, this provides a reducing environment for the analyte and prevents the graphite from oxidizing. In many systems one can interrupt the nitrogen flow during the atomization stage, which allows one to increase the residence time of the atoms in the atomizer, so that a maximum absorbance can be attained.

Newer atomizers utilize a programmable temperature control, which allows one to change the atomization temperature with time and can allow the operator to adjust the conditions to minimize interferences. Like flames, graphite atomizers are also subject to interferences. Graphite atomizer interferences are divided into two

classes, physical and chemical interferences.

Physical interferences involve the loss of atomic vapor during the atomization step. Sturgeon and Chakrabarti (75) studied the mechanism for atomic vapor loss in the Perkin-Elmer HGA 2100 graphite atomizer. They found that about 60% of the vapor condenses in the cooler ends of the atomizer, about 20% escapes out the sample entrance hole, and about 20% is absorbed into the graphite walls. The fraction of sample absorbed can be a problem, in that it will contribute to the background signal. Unless it is removed, this background signal will then be added to the next sample. Many atomizers have the capability of being heated to a maximum temperature in an attempt to rid the graphite tube of residual sample.

Chemical interferences are often more complex and in general are not well understood. Under certain conditions both cations and anions can interfere, especially if the halide is present (76,77,78,79). These interferences can be eliminated by either solvent extraction or by using the method of standard additions.

L'vov (80) was the first to try to explain the mechanism for atom production in an atomizer. In his orginal work he assumed the atoms evaporated from the surface of the graphite. More recently, other mechanisms have been proposed. Campbell and Ottaway (81) proposed a mechanism based on the reduction of metal oxides by carbon.

In addition to the evaporation and reduction mechanisms there are other reactions possible. Of course, to obtain any absorption signal at least some of the sample must be reduced to an atomic vapor. The problem of interference arises when there are competing reactions that reduce the fraction of atoms in the atomic state (82). The extent of these competing reactions depend on the sample matrix and the atomizer conditions. Initially the metal is combined with some anion. Upon atomization, the possible reactions that can occur are oxide formation, carbide formation, and evaporation of the metal salt. The metal oxide and carbide can easily be formed in the graphite or on its surface. They can also evaporate and then decompose to the metal vapor. There can also be a loss in atomic vapor by the formation of a molecule or an ion. Obviously the possibilities are complex, and it is difficult to predict the processes occurring. Despite the complexities, chemical analyses can be performed, and various parameters can be adjusted to favor the production of atomic vapor.

There are two means by which some of the atomic vapor loss can be eliminated. One method is by utilizing an impervious graphite tube to prevent the vapor from being absorbed into the graphite. The other method is to use a surface which is inert to the atomic vapor, thus preventing the formation of a metal carbide.

Baird and Gabrielian (83) lined a graphite tube with tantalum foil. The foil lining prevented atoms from forming carbides and from diffusing into the walls of the graphite, thereby increasing the signal amplitude. The foil lining also increased the lifetime of the tube and allowed the workers to use a lower atomization temperature.

L'vov and Pelieva (84) also used a tantalum foil lining and showed similiar advantages for 32 out of the 40 elements tested. Eight of the elements tested do not form low volatility carbides or intercalation metal-graphite compounds. Therefore the inertness that the tantalum gives to the graphite is of no advantage with these elements. The memory effect (residual atoms remaining after the previous atomization step) is also reduced, and again the tube lifetime is extended.

By the use of a tantalum foil lining, L'vov and Pelieva (85), were able to improve the sensitivity for 23 elements, 3 to 100 times. They were also able to reduce the atomization temperature 200^{o}C to 900^{o}C for 25 elements.

Runnels, Merryfield, and Fisher (86) found that coating the inside of the tube with carbide-forming elements such as lanthanum or zirconium prevents the formation of carbides from other elements and enhances their absorption signal. Apparently, once the carbide coating is applied, it lasts the lifetime of the tube.

Ortner and Kantuscher (87) impregnated graphite tubes with salts of tantalum, titanium, or tungsten. This enabled them to determine silicon without the silicon being lost as silicon carbide.

Other workers (88,89,90,91) have observed similiar advantages of carbide coated tubes for various metal determinations.

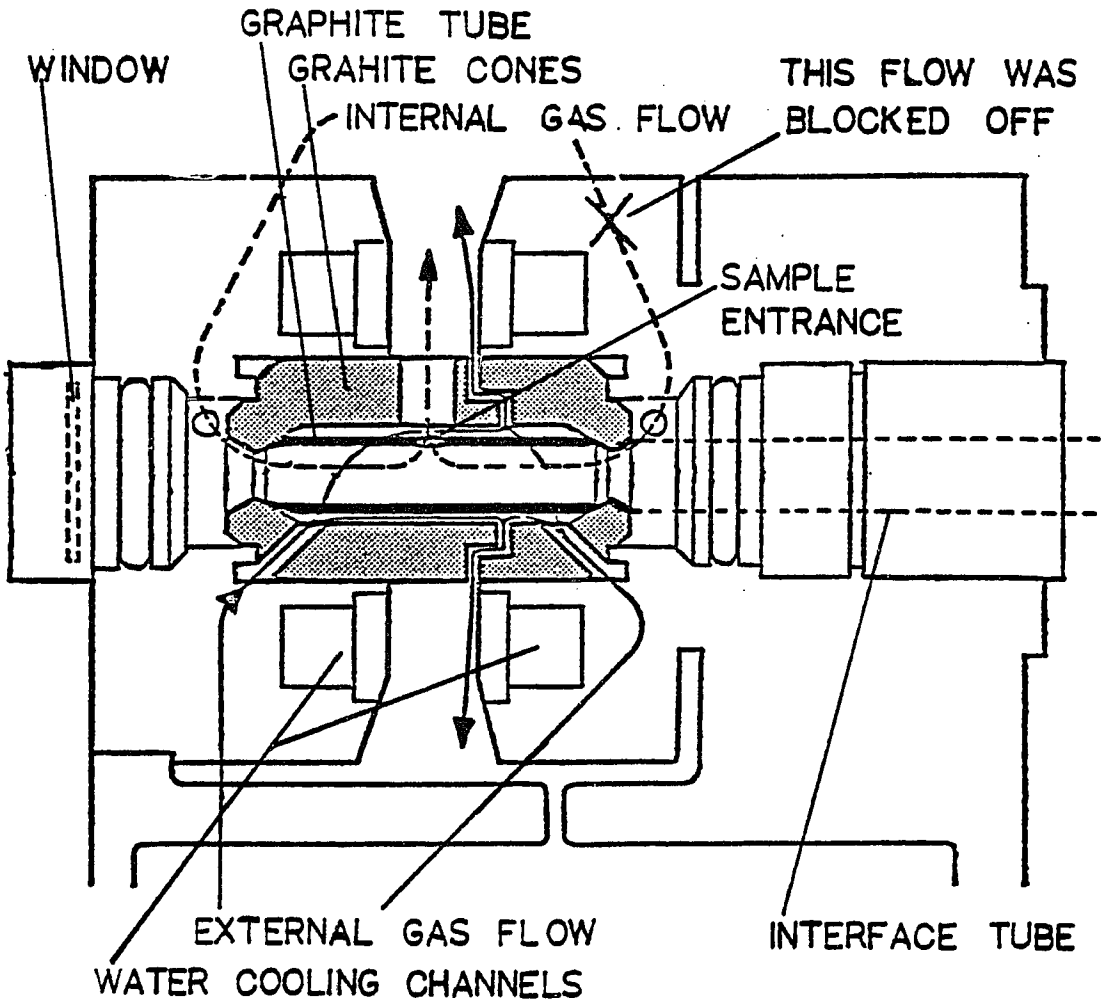
This review does not cover all the work done in the field of graphite atomizers, but it does mention some of the attempts others are making to reduce the loss of atomic vapor, either by reducing the graphite's porosity or by increasing its inertness. In this work the graphite tubes are coated with silicon carbide to form an inert surface. Because of this inert coating, sensitivity was enhanced and the degree of interference was decreased.

II. Experimental

Graphite Atomizer

A Perkin-Elmer HGA 2100 graphite atomizer was used for this research as shown in figure 1. A Perkin-Elmer HGA 74 graphite tube was used. The graphite tube is 8 mm in outer diameter and about 28 mm long. The graphite tube is inserted between two graphite contact rings that are tightly held in metal cones. Each of the metal cones has a quartz window in the end. Alternating current is conducted from one cone to the other by way of the graphite contact rings and the graphite tube. The two ends of the atomizer are held together by a spring keeping the graphite tubes firmly in place. Water is circulated through the cones to keep the atomizer cool. It was found that the temperature of the water cooling the atomizer had an effect on the signal from sulfur, so a thermometer was inserted into the water line to monitor the temperature of the water. If the water temperature exceeds 60^{o}C then a warning light comes on, and the program is stopped. An inert gas usually nitrogen, circulates inside and outside of the graphite tube, to prevent oxidation of the graphite as well as to provide an inert atmosphere for elemental reductions.

Figure 1: Cross section of the graphite atomizer. A portion of the glass interface tube, is shown, inserted into the right side. This drawing (which has been modified here), was taken from the Graphite Atomizer Instruction Manual, Perkin-Elmer Corporation, Norwalk, Ct.



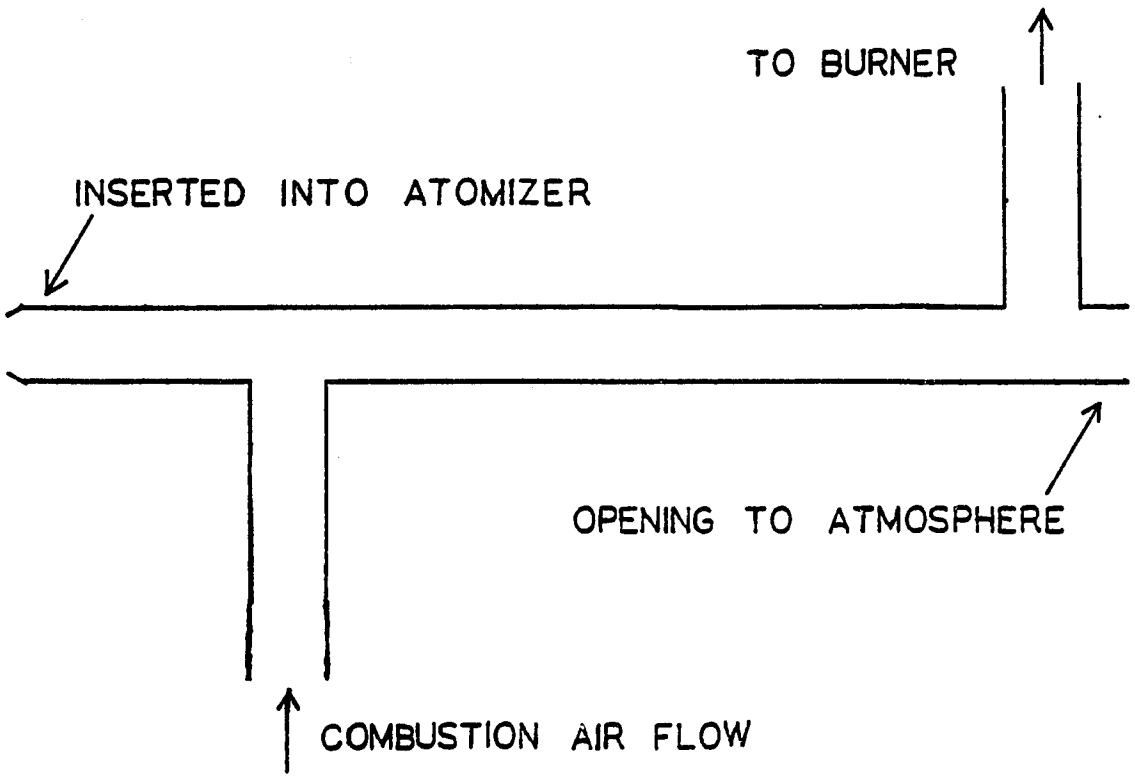
At maximum power the power supply uses about 20 amps at 220 volts which is broken down to 10 volts at about 400 amps by a step-down transformer. However, the amount of power going through the graphite tube is controlled by two silicon controlled rectifiers, whose gates are activated by pulses from the digital logic circuitry. This circuitry allows the operator to set any drying, charring, or atomization temperature from room temperature to 2800$\pm$50^{o}C that is desirable. The drying time can be set up to 120 s, charring time up to 1200 s and atomization time up to 30 s. These temperatures and times can be independently set anywhere within these limits when the program switch is pushed. A program switch is provided so that after one sets the temperature and the times desired, the heating cycle can be accurately reproduced from one sample to the next, just by pushing the program switch. A high temperature switch is provided which heats the atomizer up to 2600^{o}C, this is used to either condition a new graphite tube or to clean out any residue.

The graphite atomizer is designed to produce an atomic vapor for atomic absorption. However, for optimum coupling to the flame photometer, several modifications had to be made. The right hand window of the graphite atomizer was removed, and an interface tube is inserted directly into the end of the graphite contact ring. This interface tube shown in figure 2, is made of pyrex glass and is slightly beveled

at the end so that it makes a snug fit into the end of the graphite contact ring when held with a spring. A design used earlier, utilized a glass tube supported inside the water jacket by some GC septum material. This design was changed to reduce the dead volume between the atomizer and photometer. In the present design the glass tube is inserted directly into the graphite contact ring. However, there appeared to be no difference in signal or peak shape between the two designs.

Nitrogen flow was used not only for the two reasons mentioned earlier, but was also used to sweep the sample out of the atomizer. In atomic absorption, one desired to prolong the time the atoms were in the atomizer to achieve a larger peak absorbance. But in this instrument, one wanted to sweep the sample out as completely as possible, so that it could be analyzed in the burner. Therefore, the internal nitrogen flow was controlled by a separate pressure regulator and flow meter, Matheson Rotameter #602, which allowed a larger flow rate than when controlled by the power supply/controller. Usually a flow rate of 0.51 to 6.5 cm^3/s was used. Normally the nitrogen would also flow into both sides of the graphite tube. However when the atomizer was coupled to the burner one wanted the sample to be blown out the right end of the atomizer. Therefore the nitrogen supply entering the right side of the tube was closed off, so nitrogen entered only on the left side. The

Figure 2: Glass interface tube.



rate of external nitrogen flow, which was used merely to prevent oxidation of the graphite, was about 34 cm^3/s. No change was made in this flow rate.

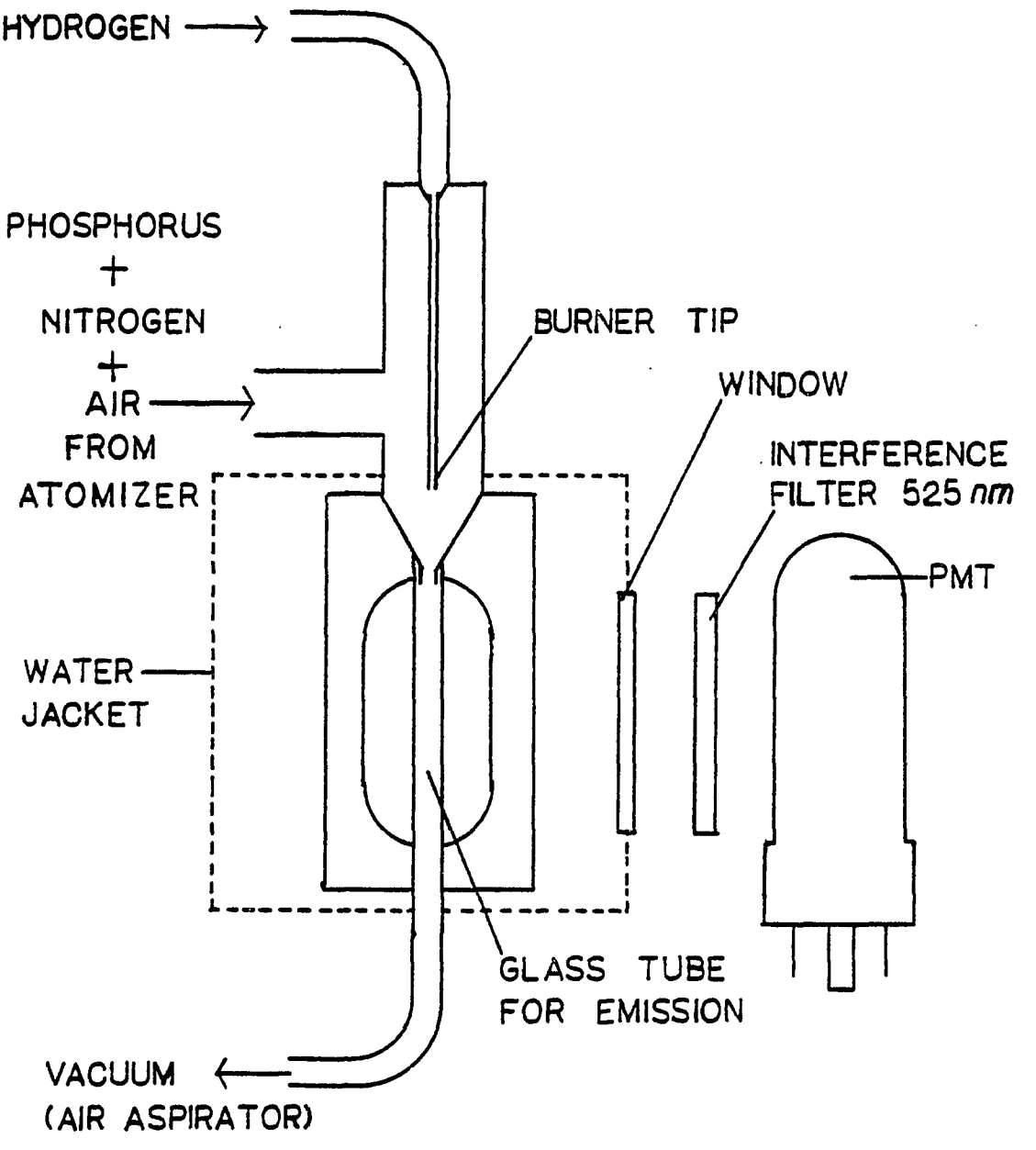
Interface Tube

As mentioned earlier, the one end of the interface tube was inserted directly into the graphite contact ring. About 3 cm from this point there was another tube connecting the main tube, through which a measured flow of air enters. This air supply was utilized by the flame so it was known as the "combustion air". Further down the interface tube the tube makes a right angle turn. This section is connected to the burner. Just after this right angle turn the tube was open to the atmosphere, thus permitting a flow of gases either in or out of the system. This interface tube was heated to about 305°C with a nichrome wire that was wrapped around it, the nichrome wire prevented moisture from condensing in the tube. Moisture was believed to dissolve the phosphorus vapor. Orginally the interface tube was heated with a plastic tape to about 50°C. Later it was thought this temperature was not high enough so nichrome wire was substituted for the plastic tape and heated to about 305°C. However, this new design proved to have no advantage over the design utilizing the plastic tape.

Burner

The present design of the burner was shown in figure 3. Hydrogen flowed down a central tube which extended down to within 0.9 cm of an orifice in the end of a stainless steel funnel. This orifice is 0.01 cm in inner diameter. Stainless steel was used here instead of the usual brass fittings, since the flame came in direct contact with this part which might result in a chemiluminescent copper emission. Nitrogen, air and the phosphorus sample came over from the atomizer and were drawn in through a larger tube surrounding the central tube. Combustion took place at the end of the central tube and the flame gases were drawn through the orifice. On the bottom side of the funnel was a Swagelock fitting that held a glass tube 5.5 cm long and 0.04 cm in inner diameter. At the bottom of the glass tube was a vacuum that was formed by an air driven aspirator. By using a pressure regulator and a flow meter (Matheson Rotameter #605) one could regulate the flow rate of air through an air aspirator which in turn controlled the pressure in the system. This controlled the amount of air and sample that was drawn into the burner. The air flow needed to operate the aspirator and to form the partial vacuum was called the "aspirator air". The purpose of the orifice (in the funnel) was to separate the actual flame which was at the tip of the central tube (the flame was

Figure 3: Burner, side view



upside down) from the chemiluminescent emission. Once one established the desired flow rates of the hydrogen and air, then the distance of the central tube from the orifice could be adjusted. The adjustment was a compromise that permitted a maximum amount of the chemiluminescent emission to extend into the glass tube, and yet a minimum amount of the flame was allowed to get through the orifice to minimize the flame background. Light from the flame itself was actually background light, since the phosphorus and sulfur compounds emitted downstream from the flame. The glass tube was mounted in a water jacket where water was allowed to circulate to cool the burner. Light from the emission shined through a window in the water jacket, then through an optical filter into a 1P21 photomultiplier tube. The optical filter was an interference filter whose maximum wavelength was at 525 nm, and had a bandpass of 10 nm at full width half maximum. A spark coil generated a high voltage that caused a spark to jump from the burner tip to the funnel. This spark was used to ignite the mixture of hydrogen and air, and was shut off once the flame was ignited.

The orginal burner was designed basically the same way as this one, except it employed air cooling and used GC septum material for gaskets to support the glass tube. There were several problems with the air cooled burner, that were eliminated when one used water cooling. One problem

with the old burner was that heat from the flame eventually got to the PMT, which caused the background current to go up after a couple of hours, this resulted in an increased baseline. After a while the gaskets also started to deteriorate; this caused air to be sucked in, which increased the flame temperature. This caused more damage and reduced the sensitivity of the emission. In the present design, the heat was carried away more efficiently by water cooling, and one could work at higher flow rates of hydrogen, air, and nitrogen. The increased nitrogen flow resulted in less atomizer background and better shaped peaks that gave better precision in the analysis. Since the overall design of the burner was more rugged, it could be operated almost indefinitely without having to change gaskets. Some workers (18,35,36,37), have observed an enhanced emission from cooled surfaces. This may be a possible advantage here, but since there were also changes in the funnel design and photomultiplier placement, the two designs could not be compared to determine if this effect occurred in this work.

Electronics

The 1P21 PMT was operated by a Princeton Applied Research, Model #280 variable high voltage power supply set at 800 volts. As shown in figure 4A, the signal from the

PMT was amplified by a Princeton Applied Research, Model #270 electrometer. The output voltage which varied as a function of time (figure 5) between 0 and 10 volts, was applied to a Heath Kit Model SR-204 strip chart recorder and also to an electronic integrator. The integrator utilized an Analog Devices Model #233K chopper stabilized operational amplifier which used an input resistor of 1 megohm and a 10 microfarad polystyrene capacitor in the feedback loop. The output was fed into an AD2002 digital panel meter.

For sulfur analysis the instrument was modified as shown in figure 4B. The square root amplifier was a Burr-Brown 4301 multifunction converter, which was wired externally to utilize the square root function. An inverter, a Nexus general purpose operational amplifier was also required to reverse polarity.

Figure 4: Electronics utilized for the determination of phosphorus, (A). Electronics utilized for the determination of sulfur, (B).

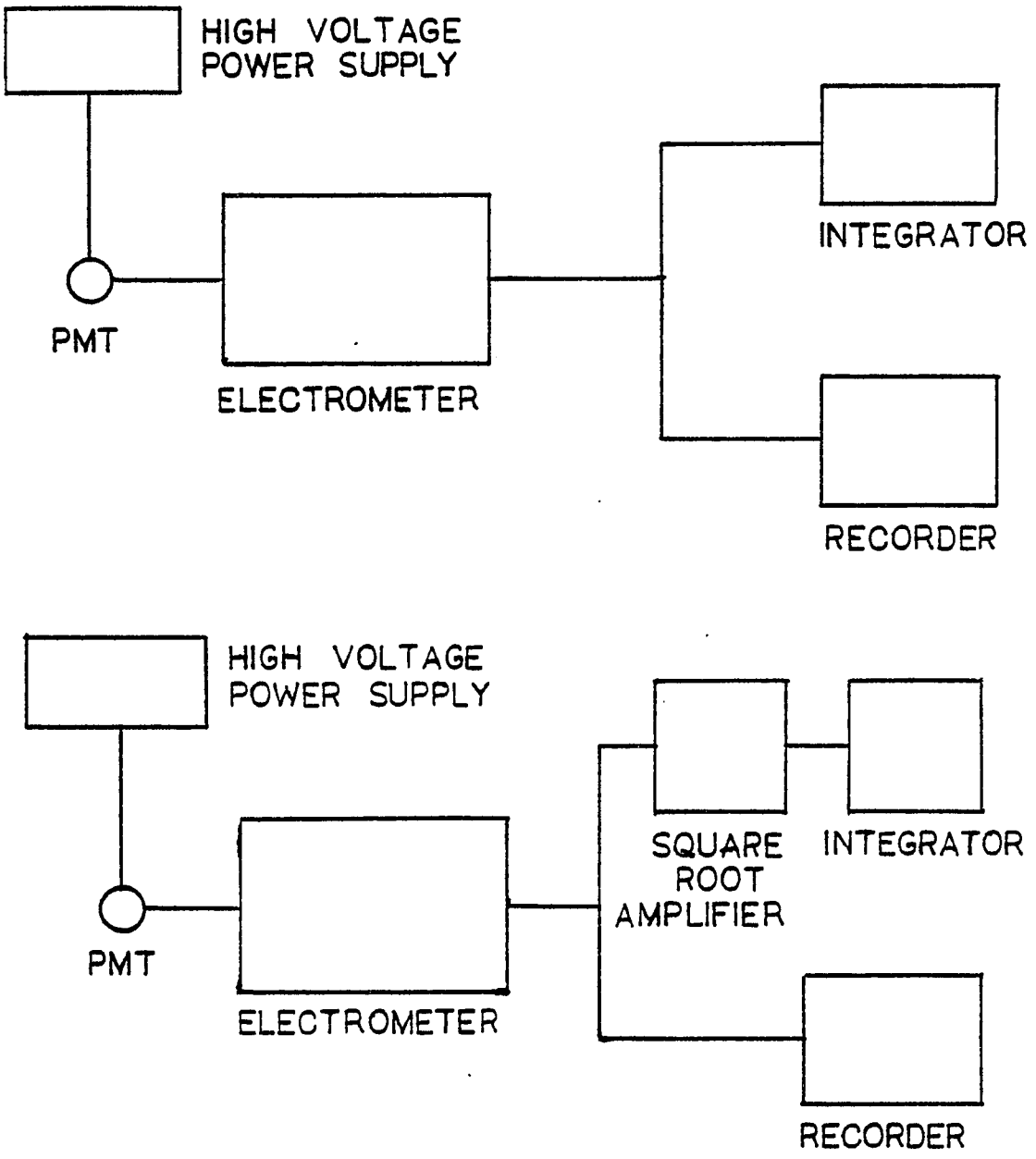
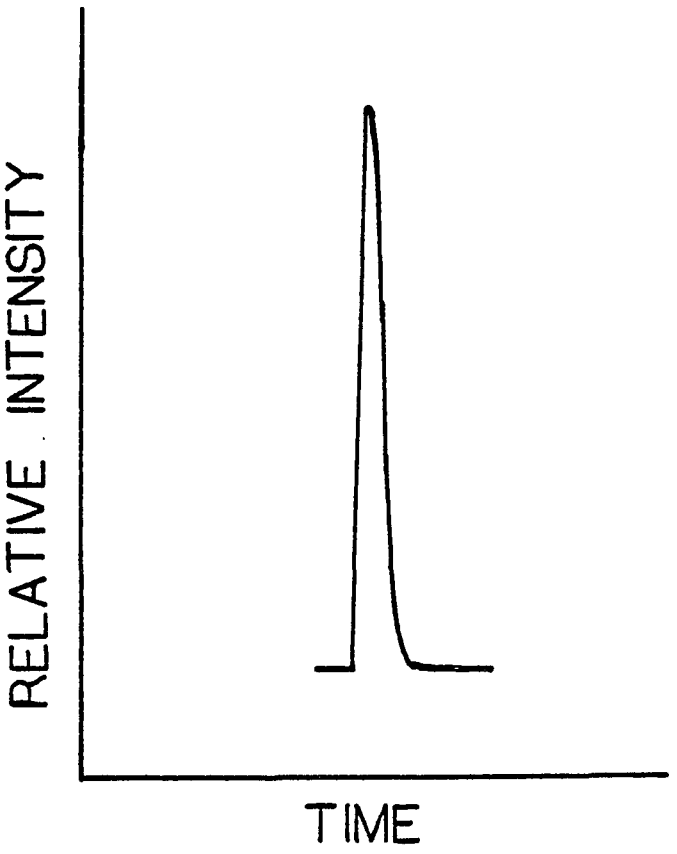


Figure 5: A typical peak for a 1 mg/L sample of phosphorus. Phosphorus is in the form of sodium monohydrogen phosphate. Atomization temperature 2500°C.



III. RESULTS AND DISCUSSION FOR PHOSPHORUS

This section is a review of several methods that were tried to eliminate the metal ion interference (92). Since the instrument used was basically the same as that employed by Campbell and Seitz (42), their work with EDTA is reviewed in some depth.

Interference studies were carried out most extensively on calcium ions for two reasons. First, calcium is commonly found in naturally occurring waters. A second reason is that calcium ion interferes more strongly than any other metal ions, and it has properties similiar to other metals. If a way could be found to eliminate the calcium metal interference, then this method would very likely work for other metals.

A general method of approach to this problem has been to use some type of a releasing agent. A releasing agent is a substance that, when added to the system, will combine with the interfering metal ion, thus preventing the metal from combining with the phosphorus compound. Releasing agents are commonly used in atomic absorption for determining calcium ion in the presence of phosphate ion (93,94). In this work a releasing agent was sought to

release calcium ions so that the phosphate ions could be detected. Unfortunately, none of the releasing agents studied was completely satisfactory. Another method of eliminating the interference was subsequently investigated.

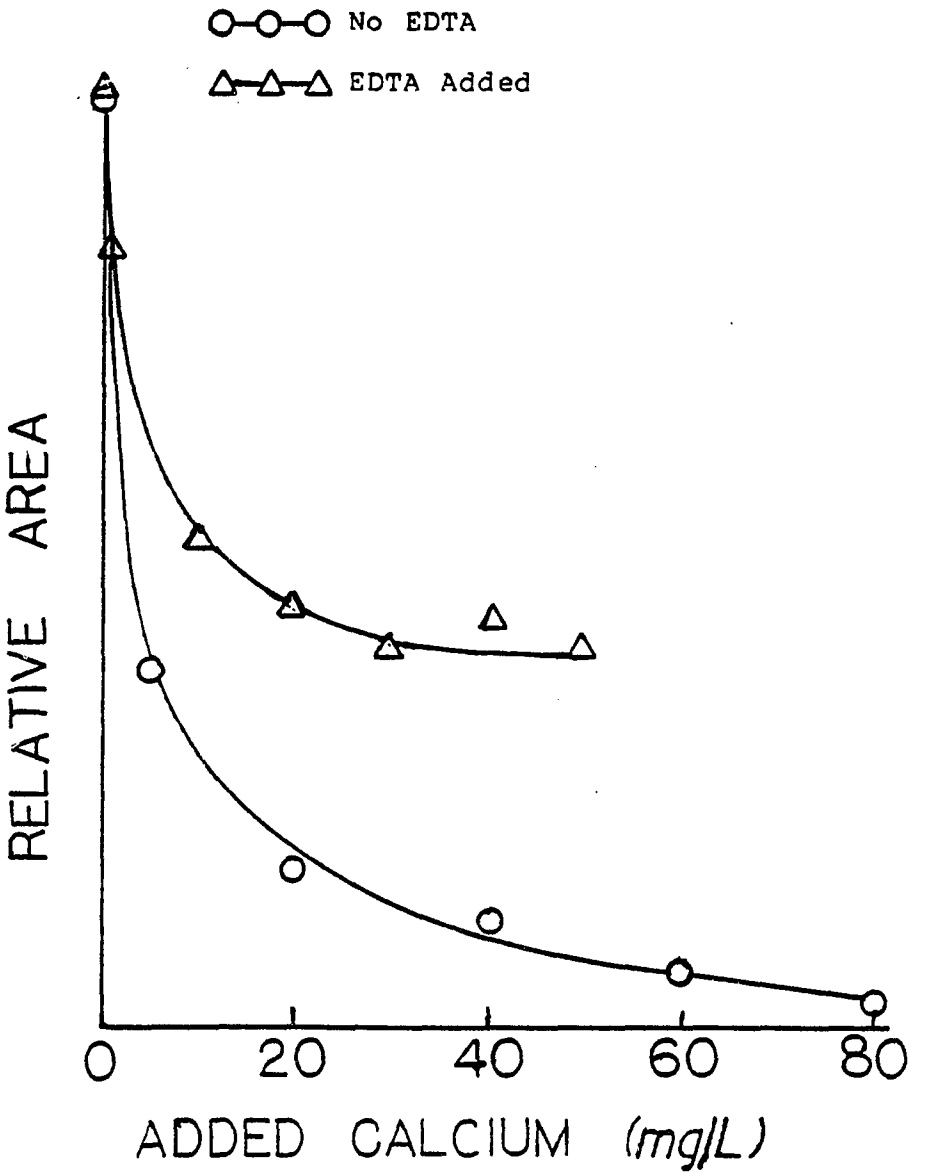
EDTA as a Releasing Agent (42)

The first attempt at eliminating the calcium ion interference used EDTA as a releasing agent. The phosphorus solution was spiked with a disodium EDTA solution before it was put into the atomizer.

The idea was to complex the calcium ion with EDTA, thus allowing the phosphate ion to be volatilized in the atomizer without associating with the calcium ion. This worked to some extent as shown in figure 6.

The peak area decreased rapidly, with an increased calcium ion concentration, up to about 20 mg/L calcium ion where it began to level off with further addition of calcium ion. The reason for this was not known, but it did show that EDTA was not a true releasing agent. If it were a true releasing agent, there would be no decrease in peak area as the calcium ion concentation increased. In a water analysis one did not know the calcium ion concentration. Therefore, it would be impossible to know where on the curve one would be working. To eliminate this problem, each water sample was spiked with calcium ions and EDTA so that the

Figure 6: Area of peak from 1 mg/L phosphorus as a function of added calcium ion in the presence and absence of 300 mg/L EDTA. Phosphorus is in the form of phosphoric acid, and calcium is in the form of calcium chloride. Atomization temperature 2300°C.



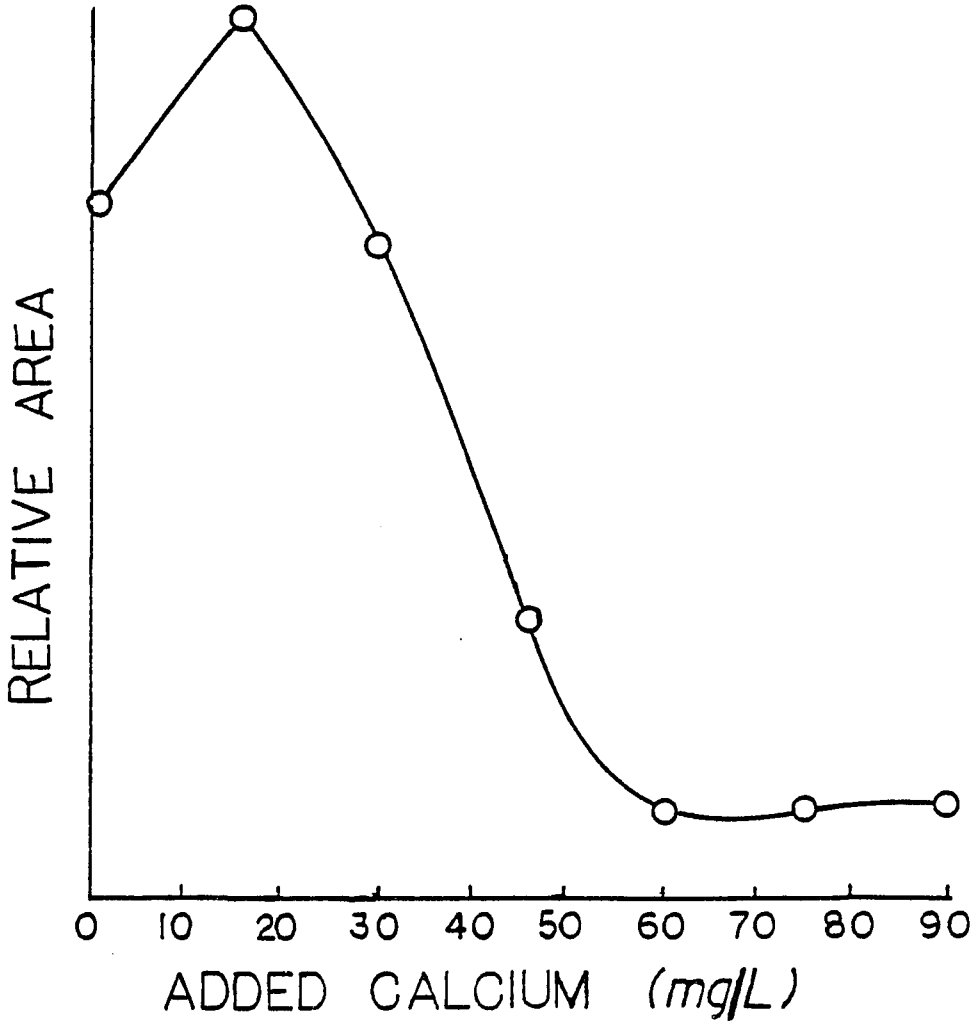
concentration was 300 mg/L of EDTA and 20 mg/L calcium ion plus the unknown calcium ion concentration. By spiking the water samples in this manner, one was assured of working on the level portion of this curve. Another disadvantage of this technique was that at higher concentrations of EDTA, the EDTA itself interfered. The reason for this was not known, but it was possible that organic decomposition products from the EDTA quench the chemiluminescent emission. This emission was known to be quenched by organic compounds (40,71).

Sodium Silicate as a Releasing Agent

Sodium silicate was also tried as a possible releasing agent. A small volume of sodium silicate solution was added to a phosphorus solution containing calcium ion before the solution was put into the atomizer. The silicate was expected to bind with calcium ions to form involatile calcium silicate rather than forming calcium phosphate. It was also thought that since sodium silicate was an inorganic compound, there would be no interference from organic compounds on the chemiluminescent emission.

Figure 7 shows a graph of peak area as a function of added calcium ion in the presence of a constant amount of sodium silicate. At moderately small calcium ion concentrations, an increase in peak area resulted, which

Figure 7: Peak area from 0.25 mg/L phosphorus as a function of added calcium ion in the presence of sodium silicate. The solution put into the atomizer contained 300 uL of a solution 1/10 the concentration of a saturated sodium silicate solution, which also contained a given concentration of calcium ion (shown below). This was then diluted to 100 mL to give a phosphorus concentration of 0.25 mg/L. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride.



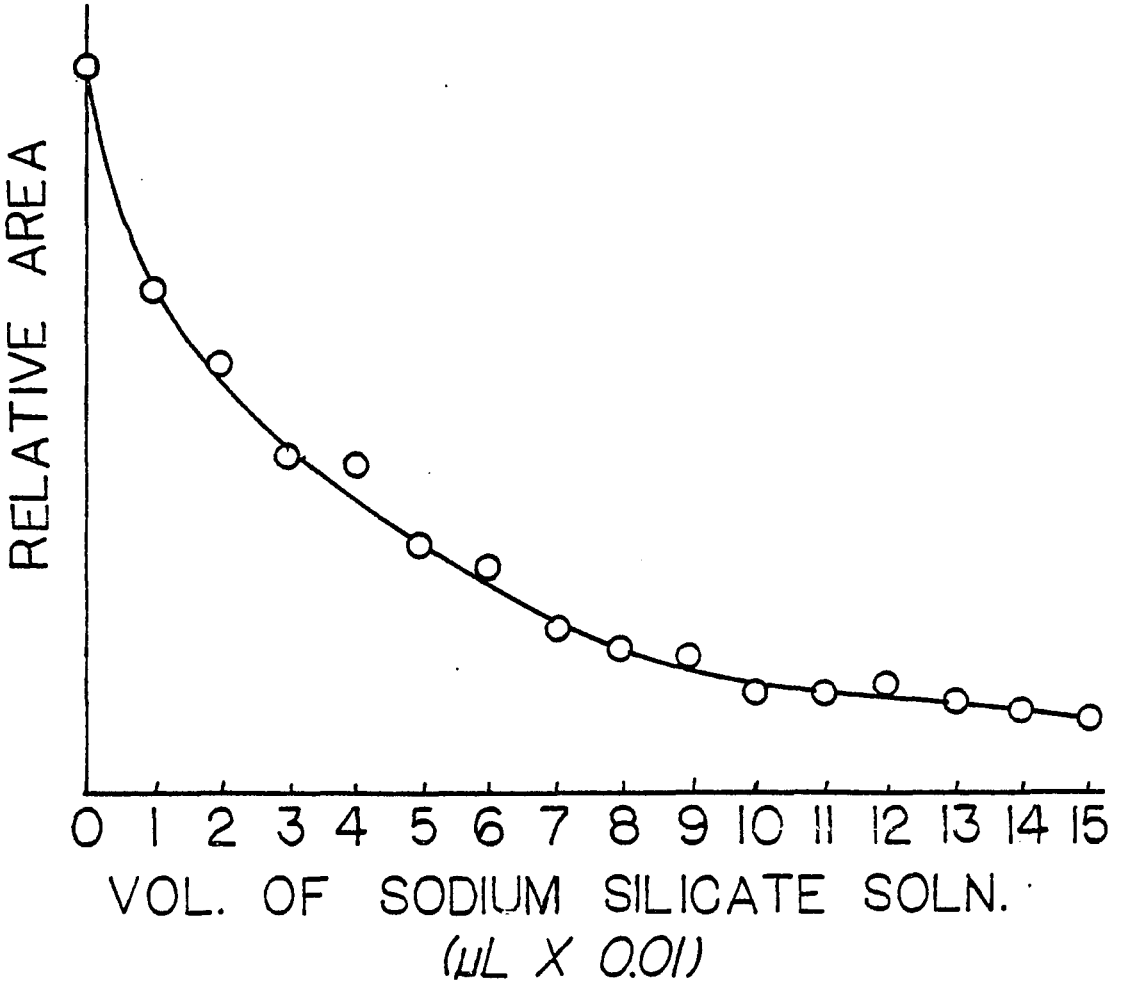
decreased to a constant peak area as the calcium ion concentration exceeded 60 mg/L. This graph indicates that sodium silicate must not act as a true releasing agent for phosphorus in the presence of calcium ion. It was also observed that sodium silicate itself gave an interference as shown in figure 8. The reason for this was not known, but it was possible that either the sodium silicate itself or some other impurity in the sodium silicate reagent was volatilized, causing the emission to be quenched.

At the present time this enhancement is believed to be the result of silicon carbide (SiC) formed in the graphite tube. Later experiments showed that when using silicon carbide-coated tubes, an enhanced signal resulted, when a phosphate solution is heated in the presence of calcium ion. If there was a silica impurity in the sodium silicate solution, then it was possible the silica reacted with the graphite causing a silicon carbide coating.

Nature of the Calcium Ion Interference on the HPO Emission

So far two releasing agents had been tried, but neither one had proven to work very effectively. The approach taken at this point was to attempt to understand the nature of the interference. If a mechanism can be determined, then this might lead to ideas as to how the instrument design or

Figure 8: Peak area from 0.25 mg/L phosphorus as a function of added sodium silicate. The solution put into the atomizer contained different volumes (shown below) of a solution, 1/10 the concentration of a saturated sodium silicate solution. Each one of these solutions was then diluted to 100 mL to give a phosphorus concentration of 0.25 mg/L. Phosphorus is in the form of sodium monohydrogen phosphate. Atomization temperature 2300°C.

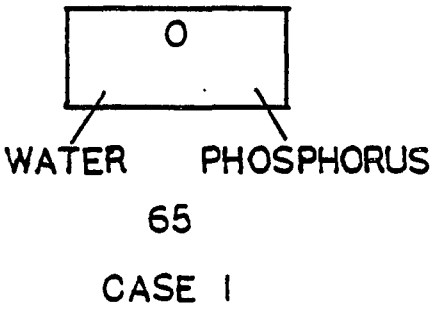


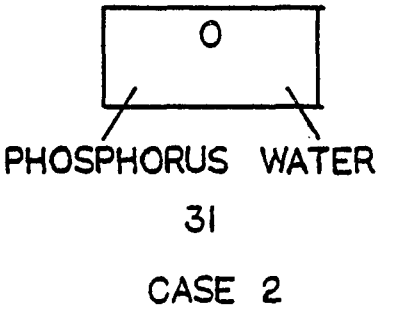
chemistry can be modified to solve the interference problem.

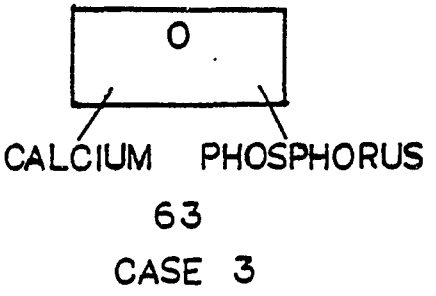
The rationale for using releasing agents was based purely on the assumption that the interference takes place in solution. However, the ineffectiveness of releasing agents suggested that the metal ion interference was perhaps not taking place in the solution phase. Instead the phosphorus and calcium may have somehow interfered in the vapor phase. An experiment was performed in an attempt to either prove or disprove this theory.

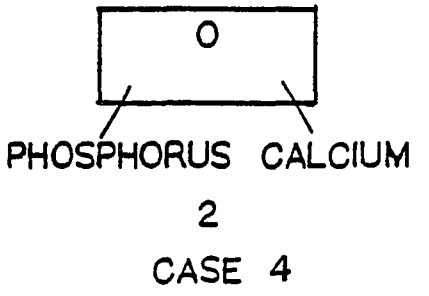
Figure 9 showed a tube with a sample hole in the center, and arrows pointing to where 2 μL of each of the following samples were placed, 10 mg/L phosphorus as Na_2HPO_4, and 100 mg/L of calcium ion as anhydrous calcium chloride. Water served as a blank. Not shown in the diagram is the interface tube to the burner. This was connected to the right side of the atomizer. The left end of the atomizer was sealed off, as always. Nitrogen gas entered through the left and swept everything out towards the right. Comparing the results of case one and two, one observes that the integrated area from case one is about twice that from case two. This is probably due to the fact that in case two the phosphorus vapor had farther to travel and some was lost along the way. This difference arose solely because of the difference in geometry. Comparing cases three and four, where calcium ion was used instead of water, one obtained a signal about 30 times greater in case

Figure 9: Solution/vapor phase experiment. "Phosphorus" refers to 2 μL of a 10 mg/L solution of phosphorus as sodium monohydrogen phosphate. "Calcium" refers to 2 μL of a 100 mg/L solution of calcium chloride. The numbers refer to the integrated peak intensity for each of the four cases. The right hand side of the atomizer is closest to the burner. Atomization temperature 2500°.









three, indicating that the geometry was not the only difference. Note also, when comparing cases two and four, that there was a 15 fold decrease when calcium ion was substituted for water. From cases one and two it appears that a factor of two arose from the difference in geometry, but in cases two and four a factor of 15 came from the interference effect of calcium on phosphorus. In cases three and four, the two effects combined to give approximately a 30 fold difference in signal. Apparently calcium ions were reduced and volatilized, and formed a cloud of calcium vapor in the tube. It appears that if the calcium ions were near the entrance of the interface tube as in case four, they interfered with the phosphorus vapor. If the calcium ions and phosphorus were in opposite positions as in case three, then the calcium vapor had essentially no effect on the phosphorus. Notice that cases one and three are essentially the same. Presumably the difference between cases three and four was due to the fact that the phosphorus volatilized sooner than the calcium. Thus in case three, it is believed that phosphorus had left before the calcium vapor.

The integrals shown here are an average of three runs for each case. Each end of the atomizer had to be opened up to introduce the sample. This made it difficult to position the samples reproducibly (in the same place each time), which in turn made good precision difficult to attain. But

a large amount of data obtained (consistent with the small sampling of data shown here) shows that the interference occurs in the vapor phase. However, in addition to the vapor phase interference that is demonstrated here, the possibility remains that there was a solution phase interference that occurs by a different mechanism. The data also show how the signal is affected by the position in the graphite tube with respect to where the phosphorus was vaporized.

If the conclusions from this experiment are correct, then it may be that if there were some way to trap or condense out the calcium vapor, the phosphorus vapor could get to the burner without any interference. It is not known whether the combination of the phosphorus and calcium vapor took place in the atomizer, the interface tube, or the burner. At one time it was assumed to be taking place either in the interface tube or the burner. This assumption seemed reasonable because, with the interface tube being cooler, the phosphorus could combine with the calcium vapor once it entered the interface tube.

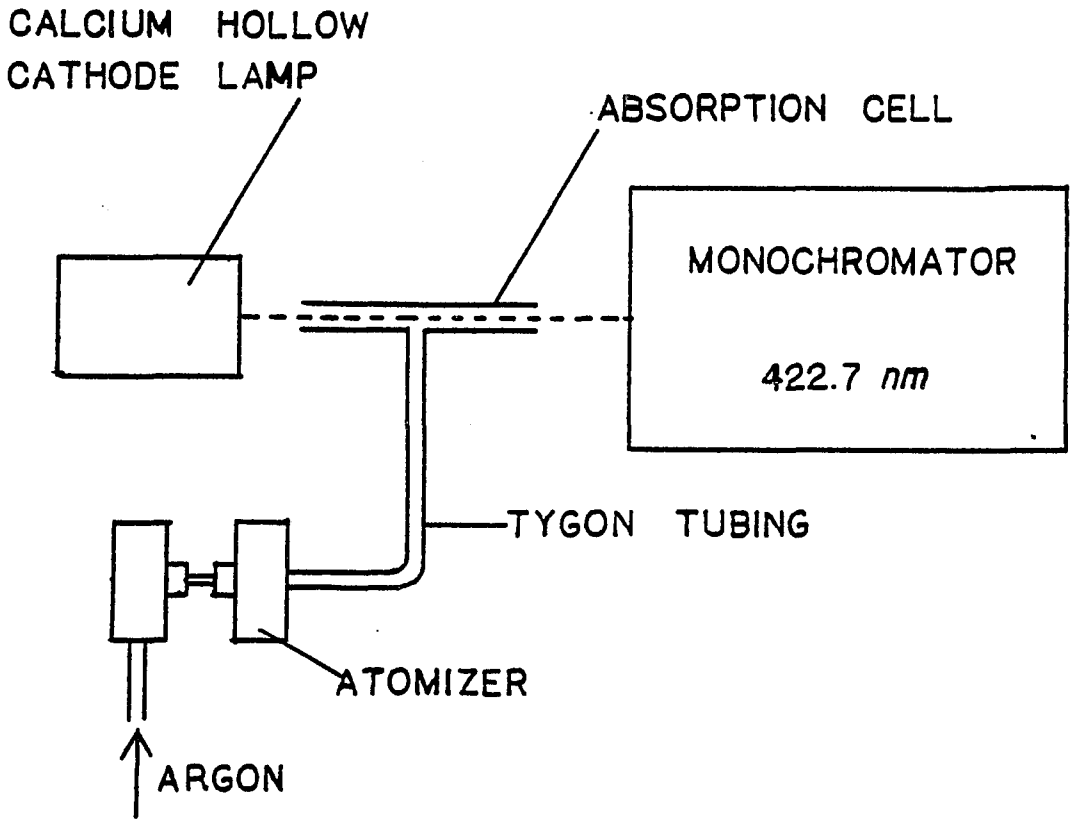
These ideas led to the insertion of a dry ice-acetone cold trap immediately following the atomizer exit. Now phosphorus solution alone, and phosphorus solution containing calcium ions were both added to the atomizer in the conventional manner. Both solutions gave a reduced signal, compared to what these same solutions gave without

the cold trap. Also the interference was still present to the same extent. The signal for both samples decreased as successive runs were carried out, strongly indicating that moisture collecting in the trap was causing the phosphorus vapor to dissolve. This whole idea was abandoned, and it was decided to try to determine just where the interference was taking place.

The following experiment was designed in an attempt to determine whether the interference took place in either one of two places: (1) the atomizer or (2) the interface tube and/or the burner. Calcium ion solutions were placed in the atomizer, and absorbance measurements were made on the amount of calcium that left the atomizer. If a significant absorbance occurred, then one would conclude that calcium vapor was leaving the atomizer and possibly entering the burner. This would mean that the interference from calcium could then occur either in the atomizer or the flame. If no absorbance occurred then one could assume that the calcium atoms were not traveling far out of the atomizer and the interference could not be taking place in the interface tube and/or the burner.

An absorption cell was placed in the light beam of a Jarrell-Ash atomic absorption instrument as shown in figure 10. A piece of tygon tubing approximately 7 cm long connected the absorption cell to the end of the atomizer. Argon carrier gas was used to sweep the sample from the

Figure 10: Atomic absorption experiment for the determination of calcium vapor leaving the atomizer.



atomizer into the absorption cell and out the ends of the cell. A calcium hollow cathode lamp was used as the source and was set at the 422.7 nm calcium line. The experiment was carried out by inserting 25 μL samples of the following solutions into the atomizer, 10, 100, and 1000 mg/L calcium ion as anhydrous calcium chloride. The samples were first dried at 110°C for 30 seconds then atomized at 2300°C for 5 seconds. The 10 and 100 mg/L calcium ion solutions did not absorb at all, where as the 1000 mg/L solution absorbed slightly (about 0.02 absorbance units). Since there was a negligble amount of absorbance, one could assume that virtually all the calcium remained in the atomizer.

Use of Silica

The results of the previous experiments provide a better understanding of the interference. At this point one knew to concentrate all of one's efforts on the atomizer and not the burner. Also, the idea of using conventional releasing agents was discarded since one now assumed that the calcium ion interference took place in the vapor phase, as opposed to an aqueous solution.

By analogy to sulfide and nitrate ions, it was believed that when phosphates were heated in a graphite atomizer, they were reduced to phosphorus monoxide. Manning and Ferndanez (95) made use of the molecular absorption of

phosphorus monoxide generated in an atomizer for doing phosphorus analysis. They found that if calcium ion was added, a maximum absorption signal from phosphorus monoxide was obtained. It was concluded from this that the interference that was observed involved an interaction between phosphorus monoxide and calcium ion in the vapor phase. When calcium phosphate was heated with silica and graphite a reaction occurred that produced elemental phosphorus (96). It was thought that elemental phosphorus might not have interacted with calcium ion in the same manner that phosphorus monoxide would, thus eliminating the interference. Cotton and Wilkinson (96) discussed the reduction of calcium phosphate, which involved the following stoichiometry for temperatures greater than 800°C.

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \longrightarrow P_2 + 3CaSiO_3 + 5CO$$

If this reaction occurred when silica was added to the atomizer then the phosphate was reduced to elemental phosphorus and the silica acted as a "flux" to combine with the calcium ion forming calcium silicate. The calcium ion was then bound in the form of calcium silicate which would be inert towards any phosphorus compound present. In the meantime, the elemental phosphorus was easily volatilized and swept out of the atomizer into the burner.

It was thought, at least initially, the most convient way to add silica to the atomizer was in a slurry. About 10 g of 400 mesh analytical reagent grade silica was put in 100 mL of water and continously kept in suspension on a stir plate. Anywhere from 25 to 100 μL of this suspension was put into the atomizer which was heated to 110°C to dry the silica, then eventually heated to 2500°C. The silica alone gave a very large background signal, when the atomizer was fired for four 5 second firings, each at 2500°C. The background signal that occurred was probably caused by phosphorus contamination of the silica. Eventually the background decreased to about 25% of its orginal value and remained at this value even when the number of heatings was increased. Despite the disadvantage of the large background, the silica did work in eliminating the interference. Identical peak areas were obtained when 25 uL each of the following solutions were put into the atomizer; one was 10 mg/L phosphorus as sodium monohydrogen phosphate and the other was 10 mg/L phosphorus as sodium monohydrogen phosphate, plus 100 mg/L calcium ion as calcium chloride. Even at up to 500 mg/L of calcium ion with 10 mg/L phosphorus the interference was still not observed, but above this concentration of calcium ion a 50% decrease in peak area was observed. The system worked well in eliminating the interference. However, after about 10 samples the interference started appearing again even at low

concentrations of calcium ion. Apparently the silica was boiling away since the atomizer was operated at 2500°, and silica boils about 2300°C. When the atomizer was at its atomization temperature, the tube was not heated uniformly. The ends of the atomizer were cooler than the center. On the end next to the interface tube, a deposit of condensed silica was observed. This gave evidence for the boiling away of the silica. This problem could easily have been solved if the tube was replenished with silica, although more firings would have to be carried out in order to get the background signal reduced. Because of the problems with background signal, and boiling of the silica, better ways were sought to keep the silica in the atomizer. The presence of silica also had an interesting effect on peak area, the area was enhanced by a factor of 2 to 3 for all samples whether they were pure phosphate, or phosphate in the presence of calcium ion.

One way to keep silica in the atomizer was to lower the atomizer temperature below 2300°C. However, this caused a reduction in sensitivity and even worse, not all of the phosphorus was swept out of the atomizer. As a result, an irreproducible amount of background signal was left in the atomizer when the next sample was to be analyzed.

Another method tried was to raise the boiling point of the silica by intimately mixing some inert material with it. It was thought that when the atomizer was heated to

2500°C, the mixture would become a solution whose vapor pressure would be low enough so it would not boil away. Equal volumes of silica and other materials such as aluminum oxide, sodium silicate, and carbon were mixed in an attempt to elevate the boiling point of the system. When melted in the atomizer, these mixtures should have formed a solution that was less volatile than that of silica alone. However, none of these mixtures worked; they would either not eliminate the interference, or else they still boiled out of the atomizer.

Use of Silicon Tetrachloride

Finally it was found that if silica was absorbed into the pores of the graphite, the volatility of the silica was reduced. A graphite tube was placed into a flask and submerged below the surface of a layer of silicon tetrachloride. A vacuum was applied with a water aspirator and the air in the pores of the graphite was drawn out. It only took a few minutes for most of the air to come out, but the graphite tube was left under the vacuum for about 15 minutes to draw off as much air as possible. During this time, the silicon tetrachloride replaced the volume that the air initially occupied. The graphite tube was then placed under water for about an hour so that the following reaction took place.

$$SiCl_4 + 4H_2O \longrightarrow Si(OH)_4 + 4HCl$$

It was believed that most of the silicon tetrachloride, (at least that near the surface) was converted to silicon hydroxide. When the tube was allowed to dry overnight and heated in the atomizer, the silicon hydroxide was converted to silica as shown below.

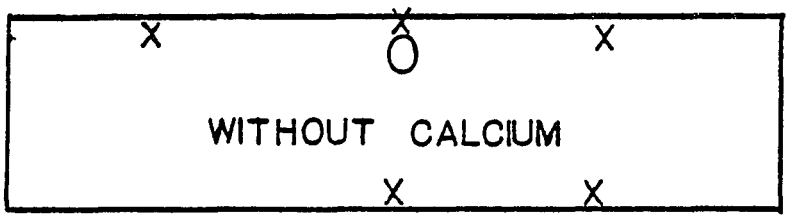
$$Si(OH)_4 \longrightarrow SiO_2 + 2H_2O$$

Another advantage of treating the graphite with silica was that if the surface of the graphite became eroded after many firings, then a fresh surface would be exposed which contained more silica. Essentially a new surface was always present because the graphite and silica are intimately mixed throughout the tube.

To prove that the silica had remained in the pores of the graphite even after repeated firings, an x-ray emission unit of an electron microscope was used to test for the presence of silicon. Two used graphite tubes were sliced longitudinally to separate the top and the bottom halves. These 4 halves were then placed in a scanning electron microscope. A beam of electrons hit an area of about 0.06 cm^2 at a depth of 1 μ surrounding each area marked x in figure 11. The count rates for a 200 s counting time, for each of the elements calcium, phosphorus, and silicon, are

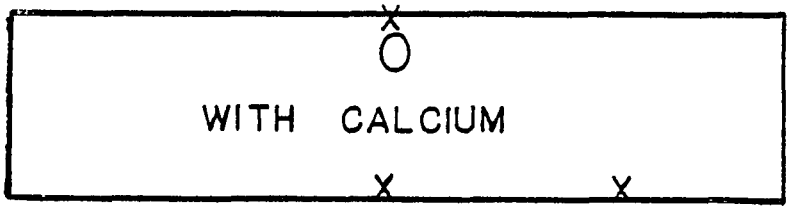
Figure 11: Electron microscope results. Numbers shown, represent the number of x-rays for each element, emitted from an area of approximately 0.06 cm^2 for 200 s.

CALCIUM	0	0	0
PHOSPHORUS	0	40	0
SILICON	450	32	9124



CALCIUM	0	0
PHOSPHORUS	0	0
SILICON	145	114

CALCIUM	0
PHOSPHORUS	0
SILICON	48



CALCIUM	9?	0
PHOSPHORUS	0	0
SILICON	69	3985

also shown in figure 11. Although the graphite tubes had about 100 samples fired in them, one can see there is some remaining silica. Apparently there was some vaporization of silica because toward the ends of the graphite tube, where it was a little cooler, there was a higher number of counts demonstrating the fact that some condensation took place. This was especially true on the right end because this was the end where the gases left the atomizer and entered the interface tube. Thus more of the silica vapor was carried in this direction than in the opposite direction which was blocked off. However, the important information gained from this experiment was that there was still silica present in the center of the graphite tube (where the sample was placed) even after a hundred firings.

Formation of Silicon Carbide

Laboratory data (from the next section and figure 12) show that the temperature at which the phosphorus is volatilized in the atomizer, (known as the appearance temperature) is much higher in the presence of silica than without it. This increased appearance temperature is not expected if silica is supposed to make it easier for calcium phosphate to be reduced. Also, in the industrial process cited in Ross, Mehring, and Jones (97), the temperature required to reduce calcium phosphate in the presence of

silica is just 1190°C under equilibrium conditions. If a temperature of only 1190°C is required, then it seems unreasonable for the appearance temperature to be much higher.

Because of these inconsistencies, the reduction of phosphate must not be an adequate explanation for the atomizer chemistry. Therefore, a mass balance on the system was performed in an attempt to establish whether or not a carbide coating actually formed. This involved a simple weighing experiment that is summarized in table 1, which was based on the assumption that the following reaction occurred.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

This reaction was proposed by Lo and Christian (98) who studied the reaction taking place in a graphite tube for the determination of silicon by atomic absorption using electrothermal atomization. Initially a new tube was weighed, permeated as described earlier; then it was dried and weighed again. The difference between the second weight and the first, was taken to be the amount of silica that has entered the pores of the graphite. Two different firings at 1500°C and 2500°C show how the weight progressively decreased as the silica was converted to silicon carbide. This gives a final weight very close to the theoretical

Table 1

Effect of Silica Treatment on Graphite Tube Weight

	Tube 1	Tube 2
Untreated tube (g)	0.7860	0.7847
Dried, Silica treated tube (g)[a]	0.8421	0.8423
After firing at 1500°C for 30 s (g)	0.8229	0.8185
Fired at 2500° for 6 s (g)	0.7889	0.7861
Theoretical weight (g)[b]	0.7897	0.7890

a. Dried at 120°C for 10 minutes and 500°C for 10 s.

b. Assuming all silica reacted to form SiC.

$$SiO_2 + 3C \longrightarrow SiC + 2CO$$

weight. This assumed that all the silica present was converted to silicon carbide, according to the above reaction. The theoretical weight was obtained by calculating the weight of carbon monoxide produced from the weight of silica, then subtracting the weight of carbon monoxide from the total weight of the silica-treated tube. This gave the weight of the tube in which the silica was orginally present, that was now converted to silicon carbide. According to these calculations the treated tube was about 5% silicon carbide. This was because the pore space made up only a relative small percentage of the total volume of the tube. From the mass balance calculations and from other bits of evidence mentioned, one could conclude that the reaction involving the formation of silicon carbide was what occurred inside the tube. The theory of how the presence of silicon carbide helped eliminate the metal ion interference will be discussed in a later section.

Analytical Characteristics of Silica-treated Atomizers for phosphorus Analysis

1. Appearance Temperature

An important observation is that the appearance temperature is higher in a tube treated with silica as opposed to a tube with no silica treatment. Figure 12 shows the data for the untreated tube which is taken from Campbell

and Seitz (42). It is not understood why the curve for the treated tube did not level off above a certain temperature as the untreated tube did. Possibly, it is because one is now using a lower internal nitrogen flow rate than that of Campbell and Seitz (42).

2. Sensitivity

Without the presence of calcium ions, the signal from phosphorus in a freshly treated tube was two to three times greater than for the same amount of phosphorus in an untreated tube. This enhancement was thought to be caused by decreased porosity in the silica-treated tube. Decreasing the porosity allowed a larger fraction of the sample to enter the burner. Less sample was lost by entering the pores of the graphite.

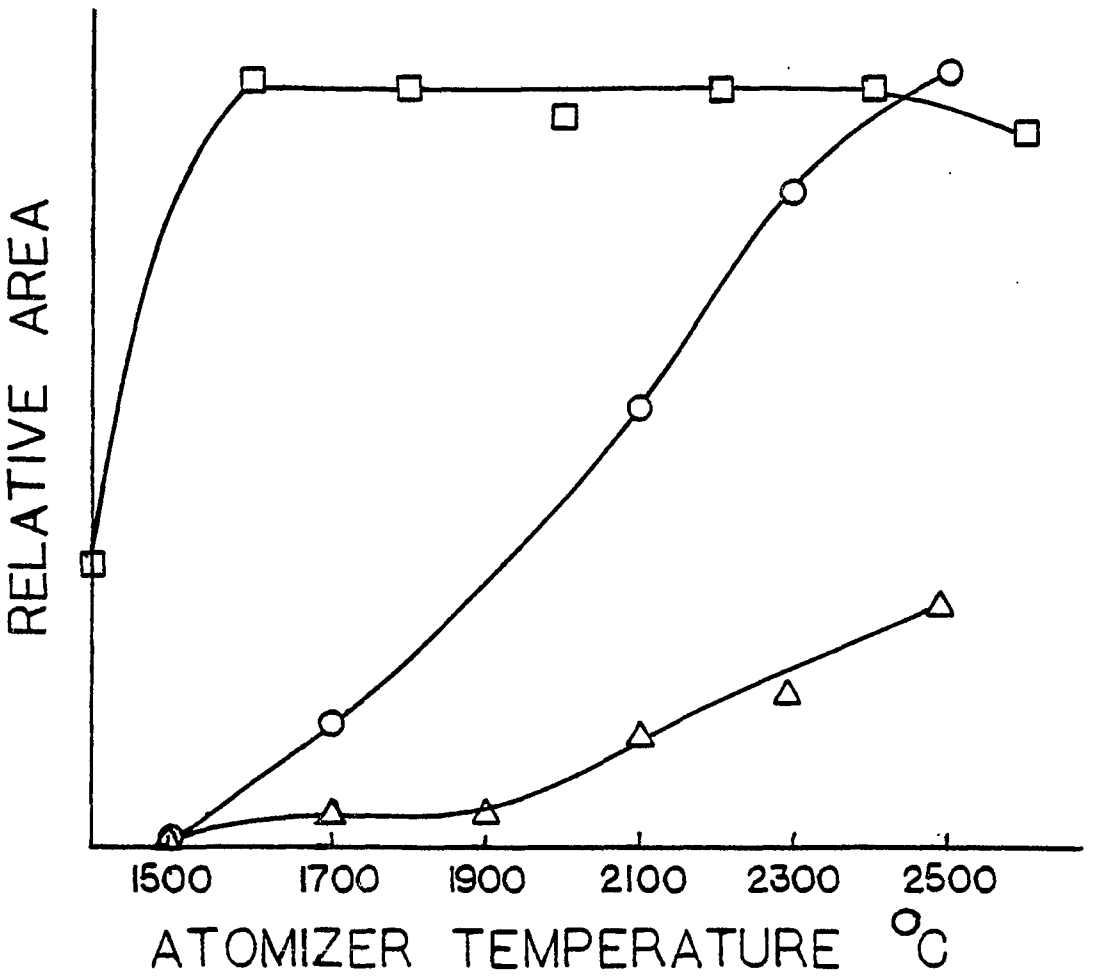
To confirm the idea that this sensitivity difference was due to porosity, the relative sensitivities were compared to a tube treated with titanium carbide and one coated with pyrolytic graphite. The titanium carbide tube was made using the same method used to make the silicon carbide tubes, only titanium tetrachloride was used instead of silicon tetrachloride. The pyrolytic coated tube was given to us by Perkin-Elmer Corporation. The sensitivity for the pyrolytic tube was about the same as that for the silica-treated tubes, which was about 1.75 times more

Figure 12: Peak area as a function of atomizer temperature. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride.

□—□—□ 1 mg/L P + 50 mg/L Ca^{++}, untreated tube

○—○—○ 1 mg/L P, silica-treated tube

△—△—△ 1 mg/L P + 100 mg/L Ca^{++}, silica-treated tube



sensitive than the titanium carbide tubes. The relative porosity of each of these three types of tubes was then estimated. Each of the tubes was utilized for a good fraction of its lifetime (80 firings) then each one was submerged in water and a vacuum was applied. The relative number of air bubbles evolved from each tube demonstrated its relative porosity. The pyrolytic tube was essentially not porous at all, where as the titanium carbide tube was more porous than the silicon carbide tube. Of course the nontreated tube was very porous. This simple test supported the theory that the relative sensitivity of these tubes was caused by differences in porosity of the tubes. These results are consistent with other work (75,83,84,85).

3. Detection Limits

The detection limit for a 25 μL sample, with an internal nitrogen flow of 6.5 cm^3/s through the atomizer was 0.04 mg/L phosphorus. This corresponded to an absolute detection limit of 1 ng. The detection limit was established by measuring the variability in background for 25 μL of water placed in the atomizer. The detection limit here was not quite as low as that in an earlier study (42), because the internal nitrogen flow was lower in this work. However, it was lower than the detection limit for phosphorus by electrothermal atomization atomic absorption

at 214 nm (99).

4. Tube Lifetime

The useful lifetime of silica-treated tubes was 100-150 firings at 2500°C for 2.5 to 5 s for each firing. This is about what to expect for an untreated tube, so the silica treatment does not extend the tube's average lifetime. Figure 13 shows the effect of aging on a silica-treated tube. A tube was repeatedly fired with either 1 mg/L phosphorus or 1 mg/L phosphorus in the presence of 10 mg/L calcium ion until the tube disintegrated. This particular tube was fired 143 times, with only a small decrease in sensitivity over the lifetime of the tube. The effectiveness of silica in the graphite was demonstrated by the fact that the signals for 1 mg/L phosphorus in the presence of 100 mg/L calcium ion remained, roughly constant, throughout the entire lifetime of the tube. An earlier lifetime study performed on an untreated tube gave a curve where the sensitivity went to a maximum in the middle of the tube's age (figure 14). Then the sensitivity dropped to less than half of the maximum sensitivity toward the end of the tube's life. The silica-treated tube gave a more constant signal throughout the whole life of the tube. This has the advantage that during a phosphorus analysis, the precision would be improved. However, this sensitivity

Figure 13: Graphite tube lifetime study, performed on a silica-treated tube. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride. Atomization temperature 2500°C.

. . . 1 mg/L P

o o o 1 mg/L P + 10 mg/L Ca^{++}, silica-treated tube

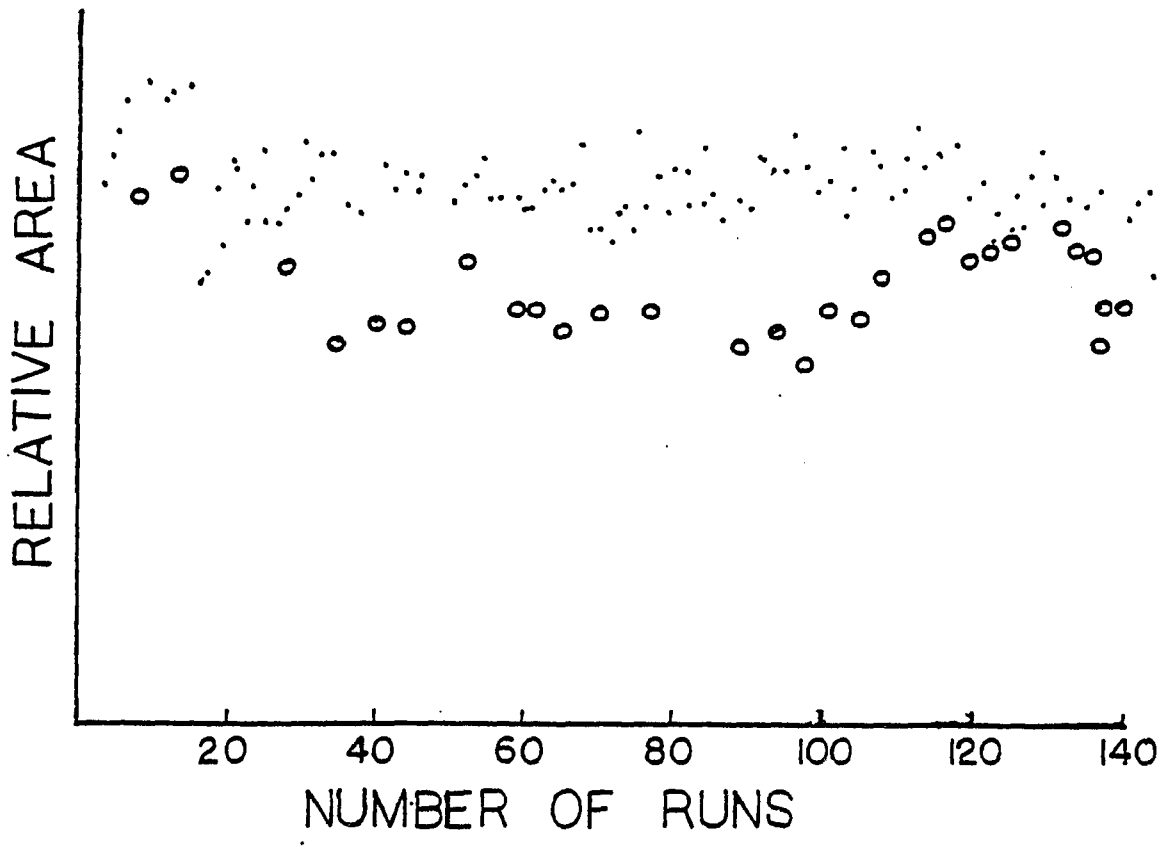
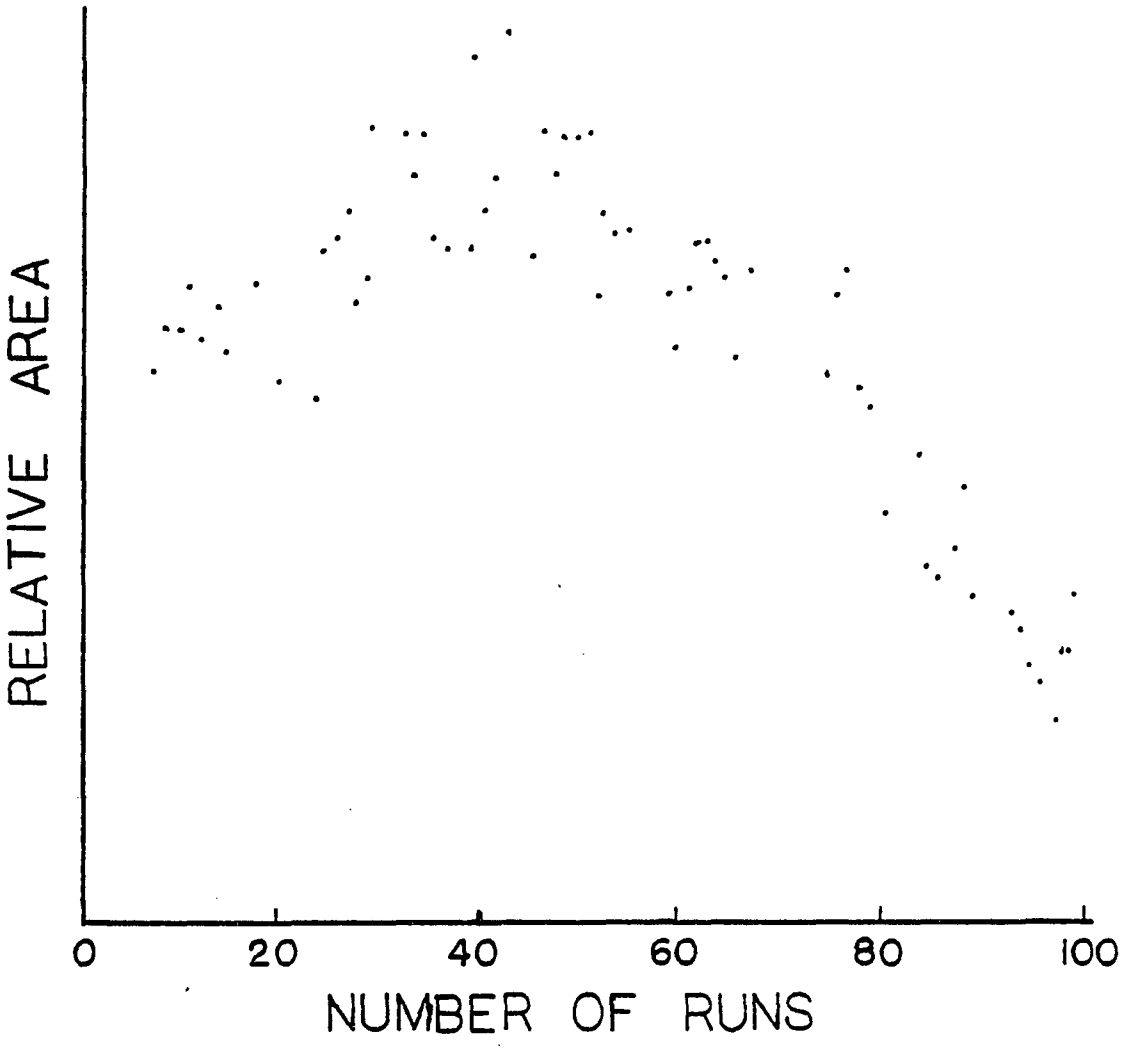


Figure 14: Graphite tube lifetime study, performed on an untreated tube. A 1 mg/L phosphorus solution was used. Phosphorus is in the form of sodium monohydrogen phosphate. Atomization temperature 2500°C.



versus lifetime behavior is not consistent with that found in all treated tubes. In some treated tubes, the sensitivity gradually decreased over the end of the tube's life, this is possibly caused by an increase in porosity as the tube got older. This variability has been observed in silica-treated tubes.

5. Precision

The data in figure 13 also give one a good idea of the precision of phosphorus measurements. Typically the relative standard deviation for 5 replicates at 1 mg/L is anywhere from 3 to 6%. Precision tended to be better in the middle of the tube's lifetime, and not as good at the beginning and the end. The major source of inprecision was probably variations in the amount of sample that entered the flame, rather than inprecision of the flame measurements itself. Possibly, a major source of inprecision was also caused by the variability of sample placement in the atomizer. As seen from figure 9 the sample position in the atomizer has a large effect on the magnitude of the signal obtained. The micropipette also contributed to the variation. The relative standard deviation for delivering 14 25 μL samples of water was measured to be 2.2%. The overall precision of the instrument improved at night time. This was probably because the electronics were more stable,

due to a decreased usage of power in the building. The decreased noise was very noticeable when using the integrator, because the baseline drifted less at night, than it would during the daytime.

6. Interferences

Table 2 shows the effects of 11 different ions on the observed phosphorus signals. At the 10 mg/L level, only calcium ion, iron III ion, and copper II ion interfered, resulting in a decreased peak area of about 10% for a 1 mg/L phosphorus solution. At the 100 mg/L level, calcium ion, chromium III ion, magnesium ion, iron III ion, and nickel ion all interfered to some extent. Copper II ion gave a slight enhancement. The reason for this was not known. Possibly copper metal vapor may have gotten into the burner and formed CuH and CuCl, these compounds could have been excited and emitted light.

Figure 15 shows a graph of relative signal versus the amount of added calcium ion. There is a sudden decrease in signal until about 3 mg/L of calcium ion then the graph levels off for a fairly large range of calcium ion concentrations. The appearance of the graph in figure 15 can change depending on which tube one uses. Sometimes the signal decreased more rapidly resulting in a decreased lower level portion. In more ideal cases, the signal did not

Table 2

Summary of Metal Ion Interferences for Phosphorus

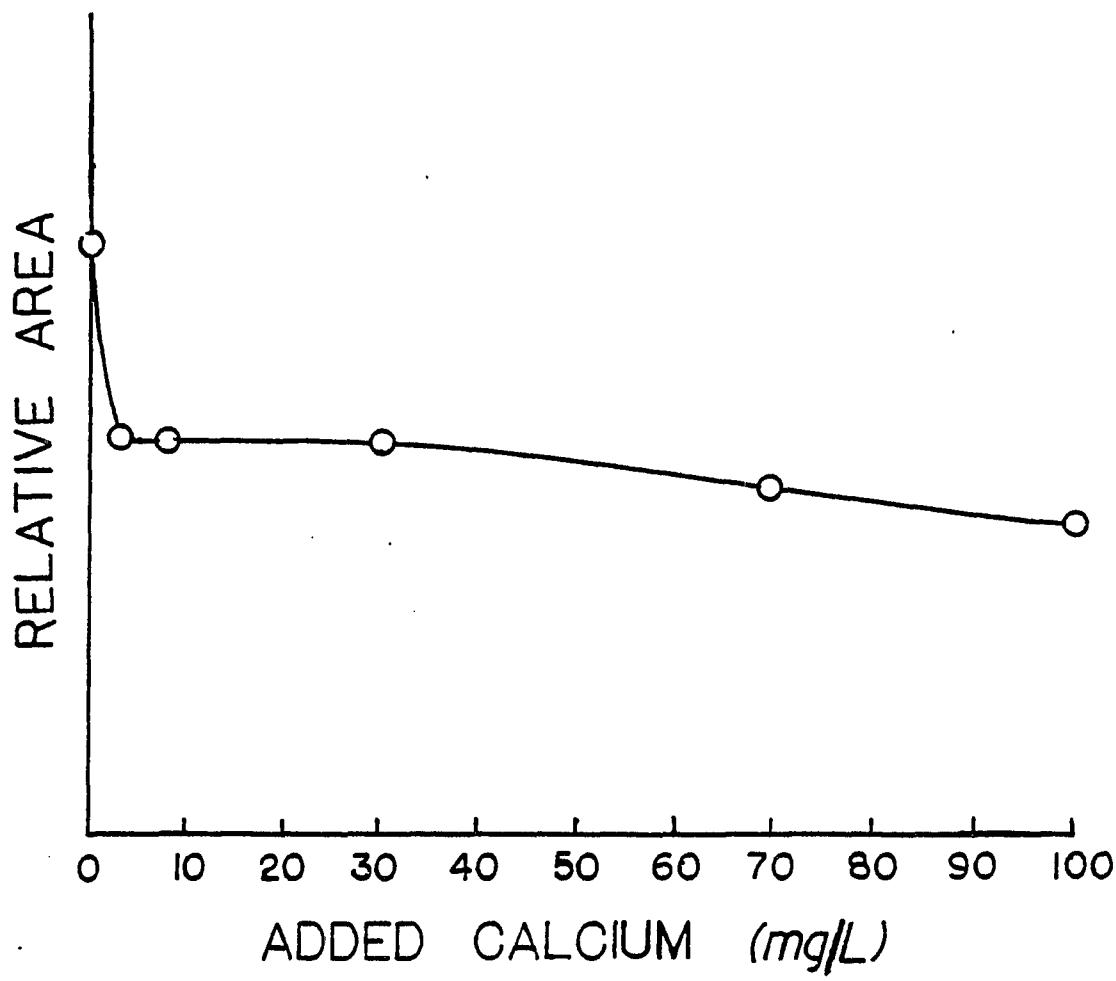
Effect of added ion on the areas of the peak for 1 mg/L phosphorus (normalized assuming the area for 1 mg/L phosphorus alone = 100).

	Relative Area	
Ion*	10 mg/L ion added	100 mg/L ion added
As III	101	97
Fe III	92	65
Cr III	104	52
Ca	89	20
Mg	101	87
Ni II	96	75
Cu II	91	120
Zn II	104	103
Bromide	96	101
Acetate	100	103
Arsenate	97	105

*Cations as the nitrate salt, anions as the sodium salt.

Data was taken at 2.7 cm^3/s internal nitrogen flow. This flow tends to reduce interferences but is responsible for higher background signals.

Figure 15: Peak area as a function of added calcium ion. A 1 mg/L phosphorus solution was used. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride. Atomization temperature 2500°C.

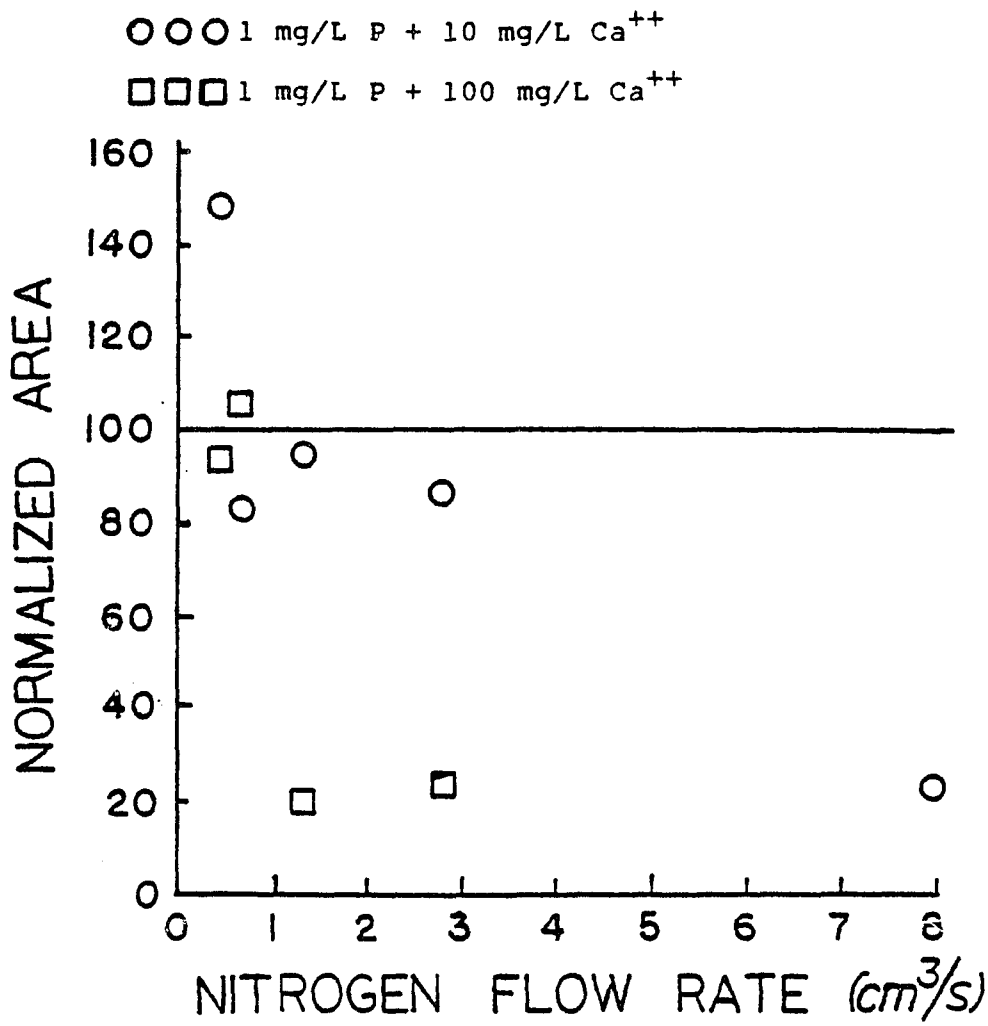


decrease at all, and may not have decreased until 200 to 300 mg/L calcium ion. The only explanation for this behavior was there were slight differences in the way these tubes were treated with silica. Notice how the calcium ion interference in table 2 differs from that shown in figure 15, yet the atomizer temperature and internal nitrogen flow rate are the same.

The extent to which calcium ion interferes was also dependent on the internal nitrogen flow. The degree of interference was reduced when the nitrogen flow rate was slowed down. However, slowing the flow rate too much caused a loss in sensitivity, and an increased background signal. The data in table 2 and figure 15 were obtained when the flow rate was 0.51 cm^3/s. This was probably the lowest flow rate one could have used without causing the background to become very large and variable.

Figure 16 is a normalized plot to show the interference effect of calcium ion on a 1 mg/L phosphorus signal as a function of nitrogen flow rate. The horizontal line represents the signal from a 1 mg/L phosphorus solution. The background has been subtracted from each reading. As the nitrogen flow rate was decreased, the interference disappeared; this was true for both levels of calcium ion. For a phosphorus solution that contained 100 mg/L calcium ion, one had to operate at even a slower flow rate in order for the interference to disappear. Unfortunately, at lower

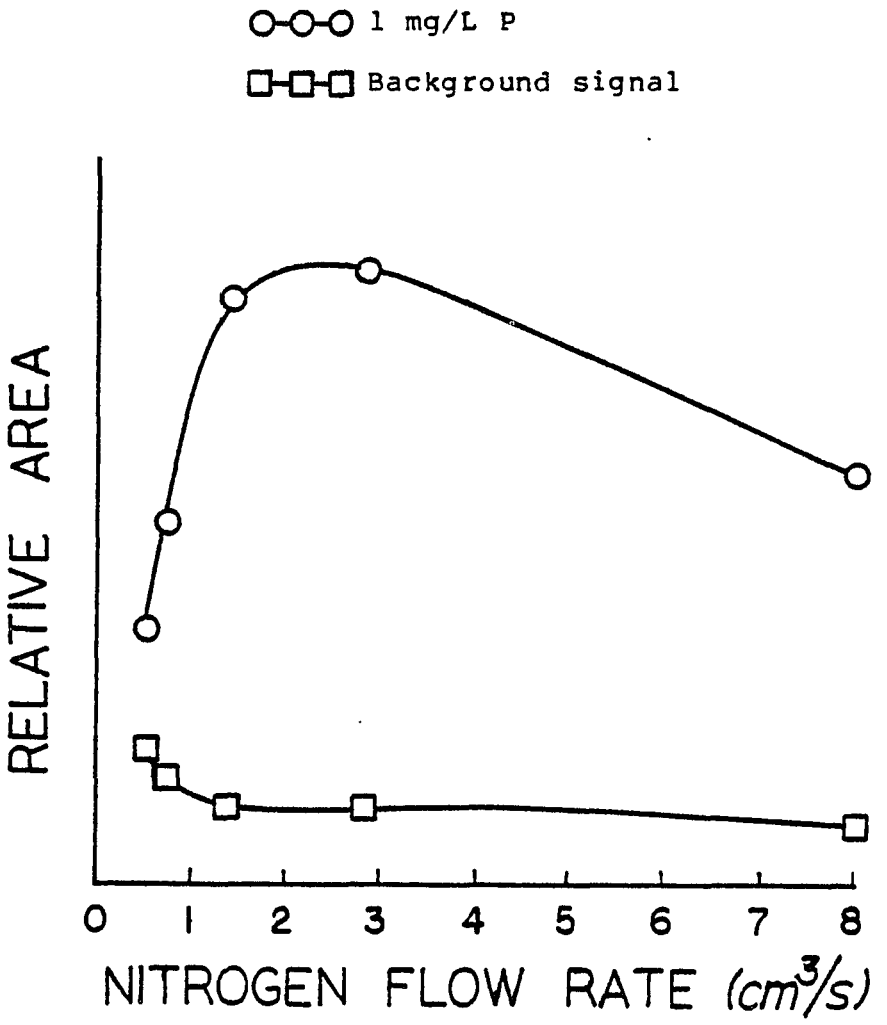
Figure 16: Normalized data to show the interference effect of calcium ion on a 1 mg/L phosphorus signal as a function of the nitrogen flow rate. The horizontal line represents the signal from the 1 mg/L phosphorus solution. This experiment was performed on a silica-treated tube. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride. Atomization temperature 2500°C.



nitrogen flow rates the precision decreased, this was probably because the background caused by residual phosphorus in the tube increased and became more variable. Figure 17 shows how the background has more than doubled going from the highest to the lowest nitrogen flow rate. Heating the atomizer to a higher temperature for a few seconds between each sample vaporized the residual phosphorus causing some improvement in precision. However, a disadvantage of carrying out this procedure was, the lifetime of the tube decreased. Sensitivity decreased by a little more than a factor of two as one changed the nitrogen flow rate from 2.9 cm^3/s to 0.51 cm^3/s, which was a disadvantage, although not a serious one. The reason for the decreased sensitivity at 0.51 cm^3/s was not understood. Possibly this decreased sensitivity was caused by a greater loss of phosphorus vapor. Since the sample was not swept out of the atomizer as quickly, it had more time to diffuse into the graphite.

Figure 12 not only shows the appearance temperature but it also shows that the degree of interference is not a function of atomizer temperature. At first, it appears that the extent of interference decreases with a decrease in temperature but this is only because of the large proportionate decrease in sensitivity. The peak areas of the samples of phosphorus containing 100 mg/L calcium ion for the three temperatures plotted from 2100° to 2500°C,

Figure 17: The signal from a 1 mg/L phosphorus solution and the background signal plotted as a function of the nitrogen flow rate. The background signal has been subtracted from the phosphorus signal. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium choloride. Atomization temperature 2500°C.

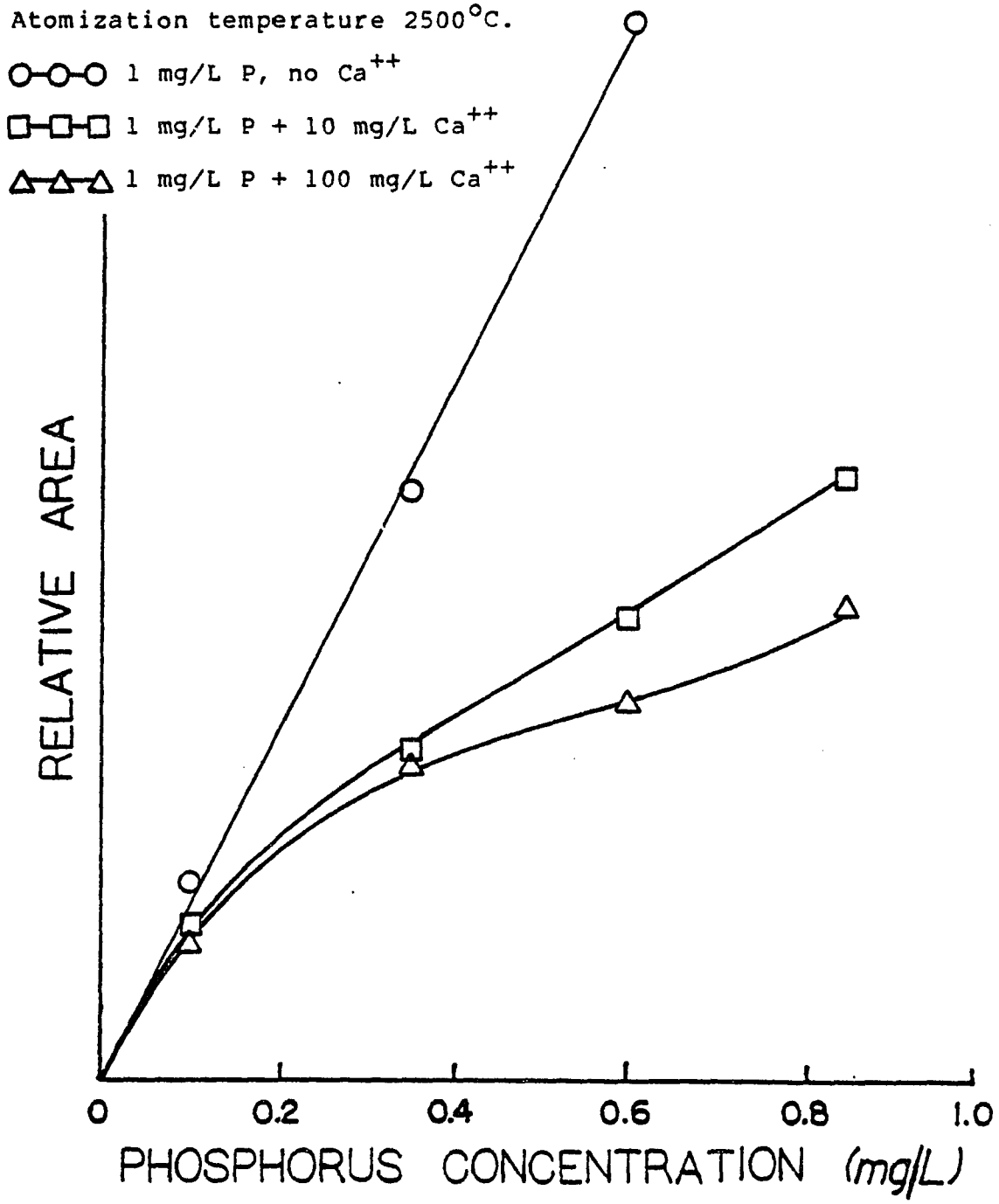


are anywhere from 25 to 31% of the peak areas of the samples containing phosphorus alone. This variation was caused by the poor precision of the instrument. At lower atomizer temperatures the precision was not as good because of the higher phosphorus background signal. Increasing the atomizer temperature helped to eliminate the background signal, but too high a temperature, especially over 2500°C caused a more rapid deterioration of the tube. According to Lo and Christian (98), the silicon carbide decomposes at 2700°C, which would definitely put an upper limit on the atomizer temperature. This also meant that the high temperature program could not be used to sweep out the residual phosphorus. In several cases where the high temperature program was used, rapid deterioration of the tube resulted.

7. Response to Phosphorus

Figure 18 shows a calibration curve for phosphorus in the presence and absence of calcium ion. In the absence of calcium ion, the curve is linear. In the presence of calcium ion, curvature resulted because of the interference effect of calcium ion. Below 0.3 mg/L the degree of curvature is slightly greater for the phosphorus in the presence of 100 mg/L calcium ion as opposed to 10 mg/L of calcium ion. This was because the 10 fold increase in

Figure 18: Calibration curves performed on a silica-treated tube. Phosphorus is in the form of sodium monohydrogen phosphate, and calcium is in the form of calcium chloride. Atomization temperature 2500°C.



concentration of calcium ion present caused a greater interference on the phosphorus signal, as was shown earlier in figure 15. Between 0.3 mg/L and 10 mg/L (the highest concentration measured), the two graphs for phosphorus in the presence of calcium ion are both linear, although their slopes are quite different. The calibration curve for phosphorus in the absence of calcium ion is linear throughout the whole concentration range. One can conclude from this data that for different phosphate ion concentrations above 0.3 mg/L phosphorus, the interference effect for a given level of calcium ion on the phosphorus signal is constant. However, the extent of interference is different for phosphorus samples containing different concentrations of calcium ion. This effect results in calibration curves of different slopes.

Mechanism of the Silica Effect

The orginal theory of how the silica eliminated the calcium ion interference via reduction is now believed to be incorrect. It is now believed that silicon carbide is formed in the pores of the graphite. The evidence for this has been cited in a previous section. However, one now needs to consider how silicon carbide affects the calcium ion interference.

From figure 12, notice that the appearance temperature for phosphate in the presence of calcium ion on graphite is 1400°C, whereas in a silica-treated tube, it is 2000°C. Therefore, it appears from figure 12, that a temperature of approximately 1400°C must be attained to reduce the phosphate to phosphorus monoxide. In the silica-treated tube the silicon carbide surface is believed to be inert, therefore no reduction reaction takes place. However, one can conclude that at the higher temperature (600°C higher) the calcium phosphate will thermally decompose into its elements. Therefore, at this elevated temperature, the interference from calcium ion is eliminated since the formation of calcium phosphate is not favored at this temperature. One does not know what chemical form phosphorus is in after the phosphate decomposes at temperatures over 2000°C, although it is probably not phosphorus monoxide. According to the results from the solution/vapor phase experiment, one knows that phosphorus monoxide in the presence of calcium react with each other, causing the interference problem.

The above explanation should also be valid for other tubes utilizing a carbide surface. A titanium carbide (TiC) tube was tried and it also gave a reduction in the extent of calcium ion interference. Ediger (99) reported the use of lanthanum III ion in atomic absorption analysis of phosphorus using electrothermal atomization. Even though

lanthanum III solution is applied with each sample, it is used in the same manner as silica is in this research, that is, forming an inert carbide surface.

This also explains why the interference becomes less when the internal nitrogen flow is lowered. At slower flow rates, the atoms remain in the atomizer longer, which means a greater fraction of the calcium phosphate has time to decompose.

One could predict that the surface of the pyrolytic graphite tube is not inert, and that there would be a larger interference problem with pyrolytic graphite. This was found to be true. A 1 mg/L phosphorus solution containing 10 mg/L calcium ion gave a signal only 13% of what it should be with just 1 mg/L phosphorus. When this same experiment was performed on silicon carbide and titanium carbide tubes, the calcium interfered to a much smaller extent.

As noted in the introduction to electrothermal atomizers, many workers utilized a carbide-coated surface so that the analyte will not react with the graphite tube and be lost. In this work a carbide coated tube is used so that the analyte will not react with the graphite forming phosphorus monoxide, otherwise the phosphorus monoxide reacts with the calcium, causing a loss in signal.

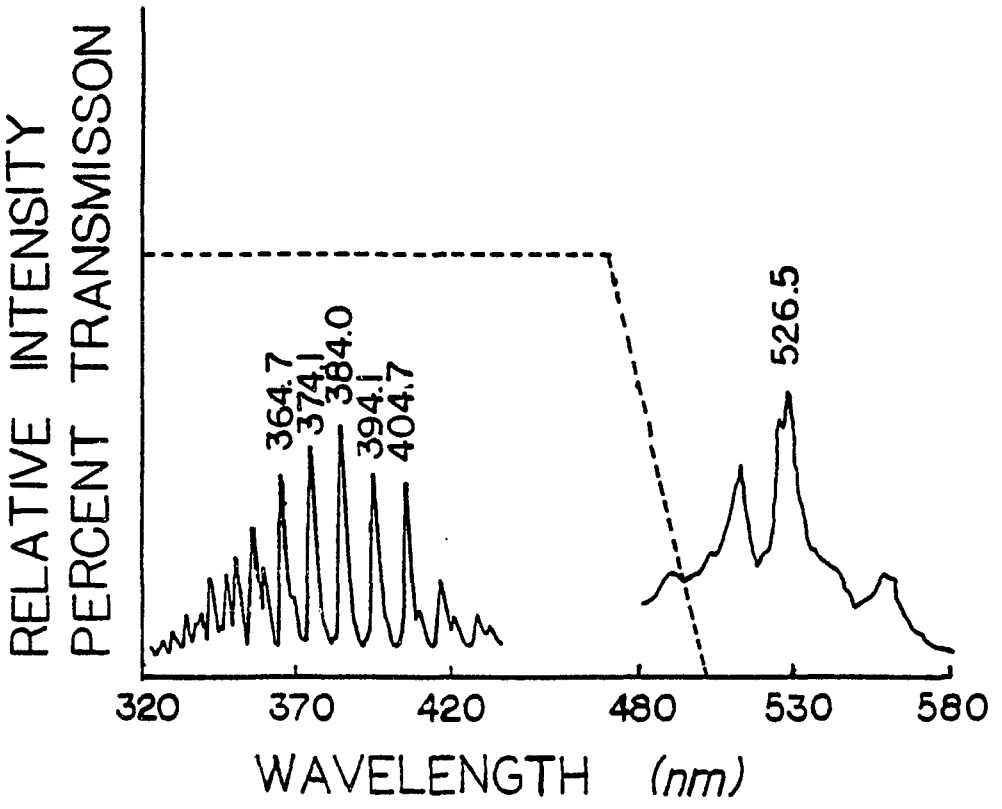
IV. RESULTS AND DISCUSSION FOR SULFUR

Instrument Modification

In the conversion of this instrument for sulfur analysis, one had to make two changes. One change was the type optical filter used. The maximum bands for the molecular emission of sulfur were at 384 nm and 394 nm. These bands were short enough in wavelength that none of the phosphorus bands interfered. Therefore, a broadband filter was chosen that had a bandpass from about 450 nm, all the way down to the UV cutoff for glass. As shown in figure 19, both the HPO and S_2 emission spectra are shown with the transmission spectrum of the filter. The advantage of a broadband filter was that more of the molecular emission bands for sulfur were included in the wavelength range observed. This gave a greater sensitivity.

If one plots the log of the sulfur emission versus the sulfur concentration (at concentrations lower than 10 mg/mL), then the resulting graph is a straight line whose slope is approximately two. This means that the square of the sulfur emission intensity is proportional to the concentration of sulfur. If one measured the sulfur emission intensity and took the square root of the

Figure 19: Molecular emission spectra of phosphorus and sulfur. The dotted line shows the relative percent transmission for the optical filter used for sulfur analysis.



electronic signal from the PMT, the output would be proportional to the sulfur concentration. This square root function was performed by a Burr-Brown Multifuction Converter that was wired in the square root mode. The output of the square root amplifier was then integrated as shown in the block diagram of figure 4B.

As with phosphorus, it was decided to use area as a measure of concentration rather than peak height. In most cases with sulfur, the peak shape did not change much. In a few cases however, the peaks were a little broader when calcium ion was present. Because of this broadening, the peak height could not be used for determining the concentration, whereas the area can be used for analytical purposes.

Thermal Effects on the Sulfur Signal

When the work on sulfur was first started, experimental results were not reproducible from one day to the next. The problem was that the water flowing through the atomizer and the burner was not at the same temperature each day. As a consequence, an experiment was devised to determine the effect of water temperature on the sulfur signal.

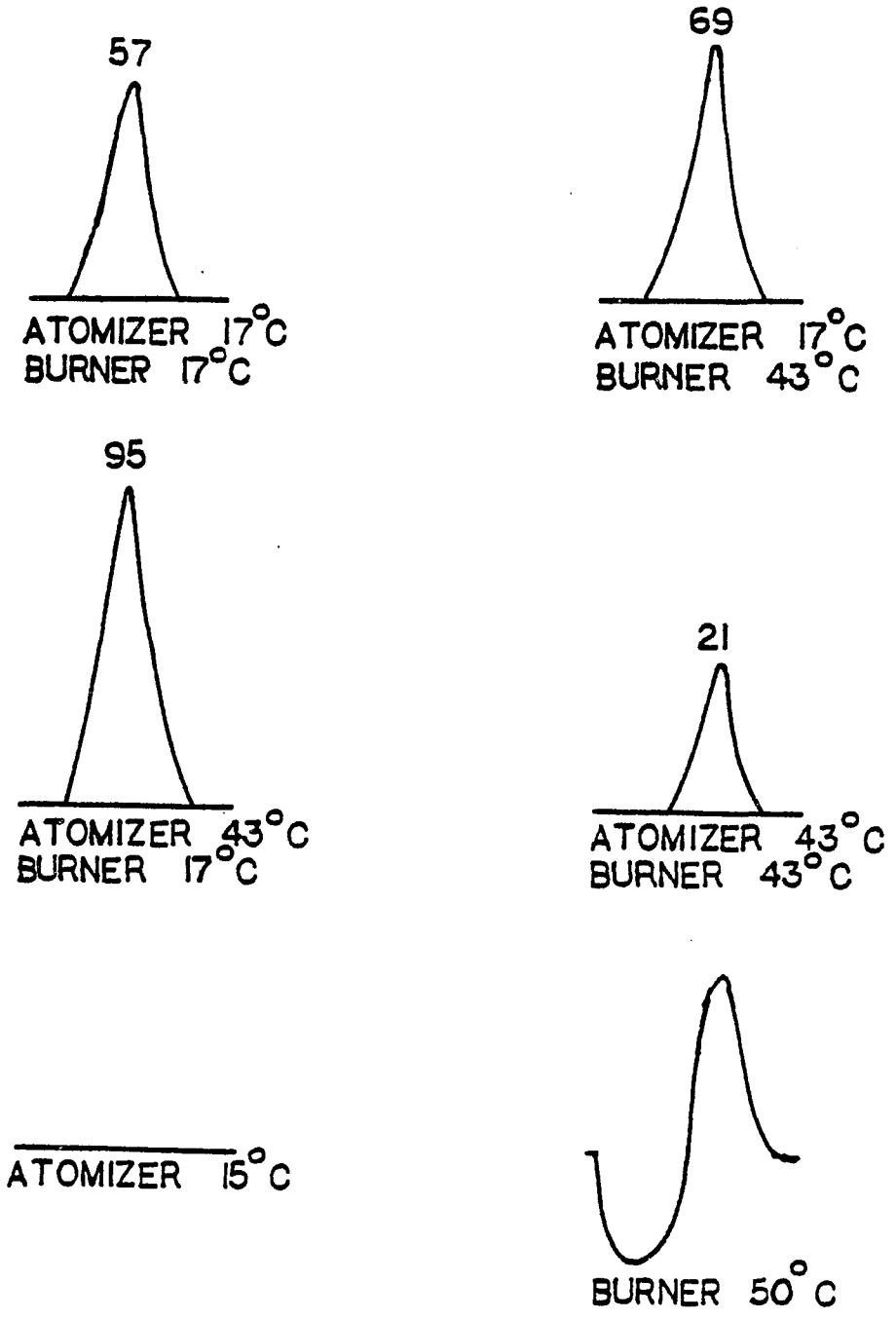
This instrument had two independent water systems to cool both the burner and atomizer. Therefore, to investigate the effect of the water temperature on the

sulfur signal, one varied the temperature of each system.

To simplify the experiment, only two different temperature levels were selected for each cooling water system. If the burner water temperature approached 50°C, the peak became distorted, causing a valley before the peak as shown in figure 20. This distortion caused extremely poor precision because it made it difficult to start the integrator at zero. This was because the baseline was essentially vertical right before the peak. It was not understood why the valley occurred before the peak. If the atomizer water temperature was about 15°C or below, then the sulfur signal disappeared. It was believed that moisture from the sample condensed inside the atomizer cone, causing the sulfur vapor to dissolve. When considering these factors one decided to set the high level at 43°C, and the low level at 17°C.

The 4 peaks at the top of figure 20 illustrate an outline of the experiment. The water temperature of both the atomizer and the burner are shown below each peak. Above each peak is shown the average of the integral obtained when a 5 mg/L sulfur solution is analyzed. There appear to be considerable differences in the peak areas obtained between the high and low temperature settings. However, the data shown here is only approximate, because at this time the square root amplifier was not yet put into operation. As a result, the precision is extremely poor,

Figure 20: Effect of the cooling water temperature on the sulfur signal. The integral listed above each peak corresponds to 5 mg/L sulfur from a sodium sulfate solution.



30-50% relative precision. In view of this poor precision, the change in signal as a function of water temperature (as seen in figure 20) is not great enough to be statistically significant. Therefore, one hesitates to predict how much the changing water temperature affected the sulfur signal, even though there appears to be some effect. However, one decided to keep a better control of the water temperature before proceeding with other experiments.

It was not too difficult to attain a fairly good temperature control, because other than the use of a hot water heater during the colder months of the year, no other temperature controls had to be provided. In practice, if one let the water flow from a nearby tap for about ten minutes before starting the instrument, then the temperature never varied more than 2 to 3^{o}C for periods of time up to several hours. This procedure was carried out each time the instrument was put into operation.

In order to check for any other possible inconsistencies, it was decided to repeat a number of experiments on two separate days while keeping the water temperature constant. Once this was performed, there were no more inconsistent results. Therefore, one concluded that the water temperature must have some affect on the various experiments performed. Even though the quantitative data on the effect of temperature is ambiguous, it is believed to be safe to conclude that a change in water temperature must

have some effect on the sulfur signal.

It is strongly suspected that prior to the water temperature control, water flowing through the atomizer and burner was initially about 10°C warmer for the first hour of operation. After this period of time, water flowing through the tap was cooler because then the water started coming in from outside the building. If an experiment was performed during the first hour, then it could yield different results than if it was run two hours later. Since on two different days the experiments were usually repeated in a different order, the temperature could easily be 10°C different for two different runs of the same experiment.

Appearance Temperature

Figure 21 shows the appearance temperatures for two different 5 mg/L sulfur solutions. One solution contains 5 mg/L sulfur; the other solution consists of 5 mg/L sulfur in the presence of 100 mg/L of calcium ion. Both of these solutions contain sulfur in the form of sodium sulfate. The appearance temperature for the first solution is at 1700°C which is 600°C lower than that of the latter solution containing calcium ion. This is reasonable since the presence of calcium ion is expected to cause the formation of calcium sulfate which is less volatile than sodium sulfate. The constant signal below 2300°C for the sulfur

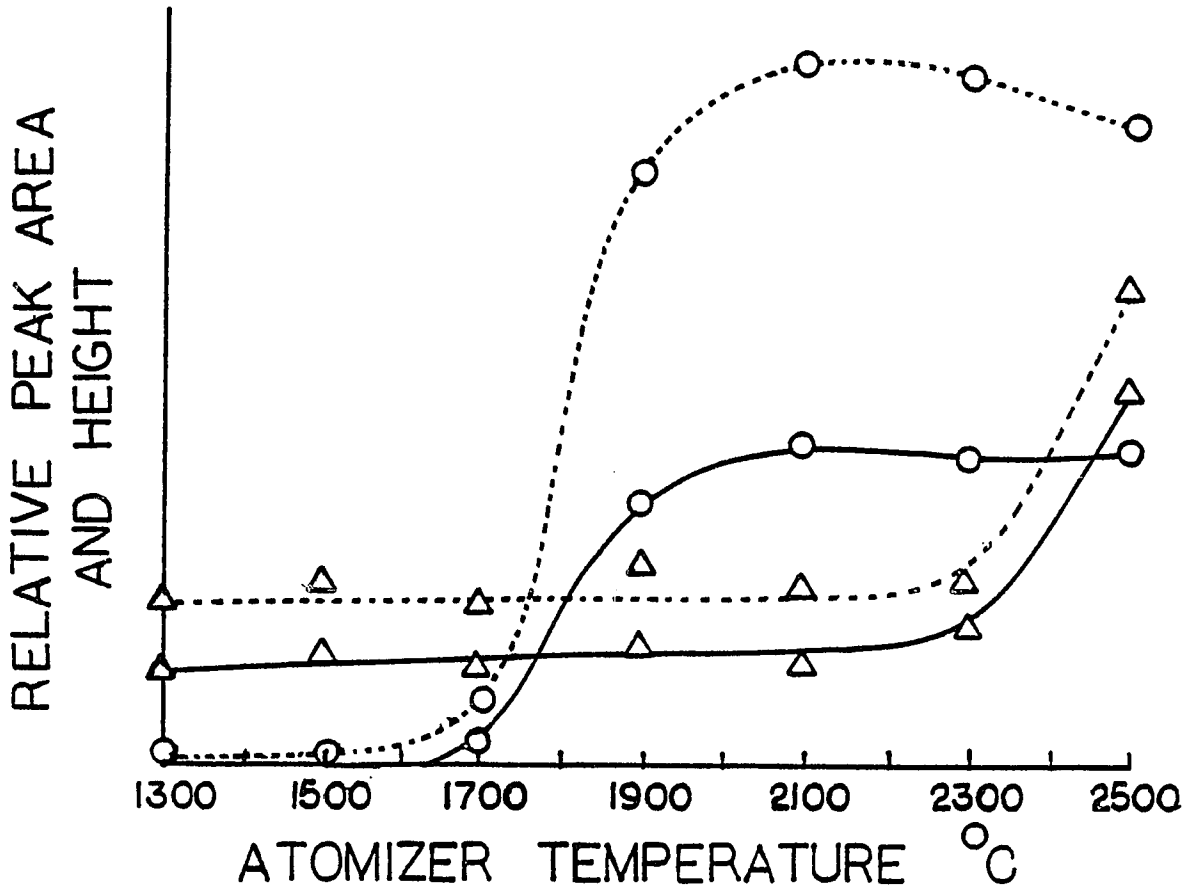
Figure 21: Peak area and peak height as a function of the atomizer temperature. Sulfur is in the form of sodium sulfate, and calcium is in the form of calcium nitrate.

○···○···○ 5 mg/L S, peak height

△···△···△ 5 mg/L S + 100 mg/L Ca^{++}, peak height

○—○—○ 5 mg/L S, peak area

△—△—△ 5 mg/L S + 100 mg/L Ca^{++}, peak area

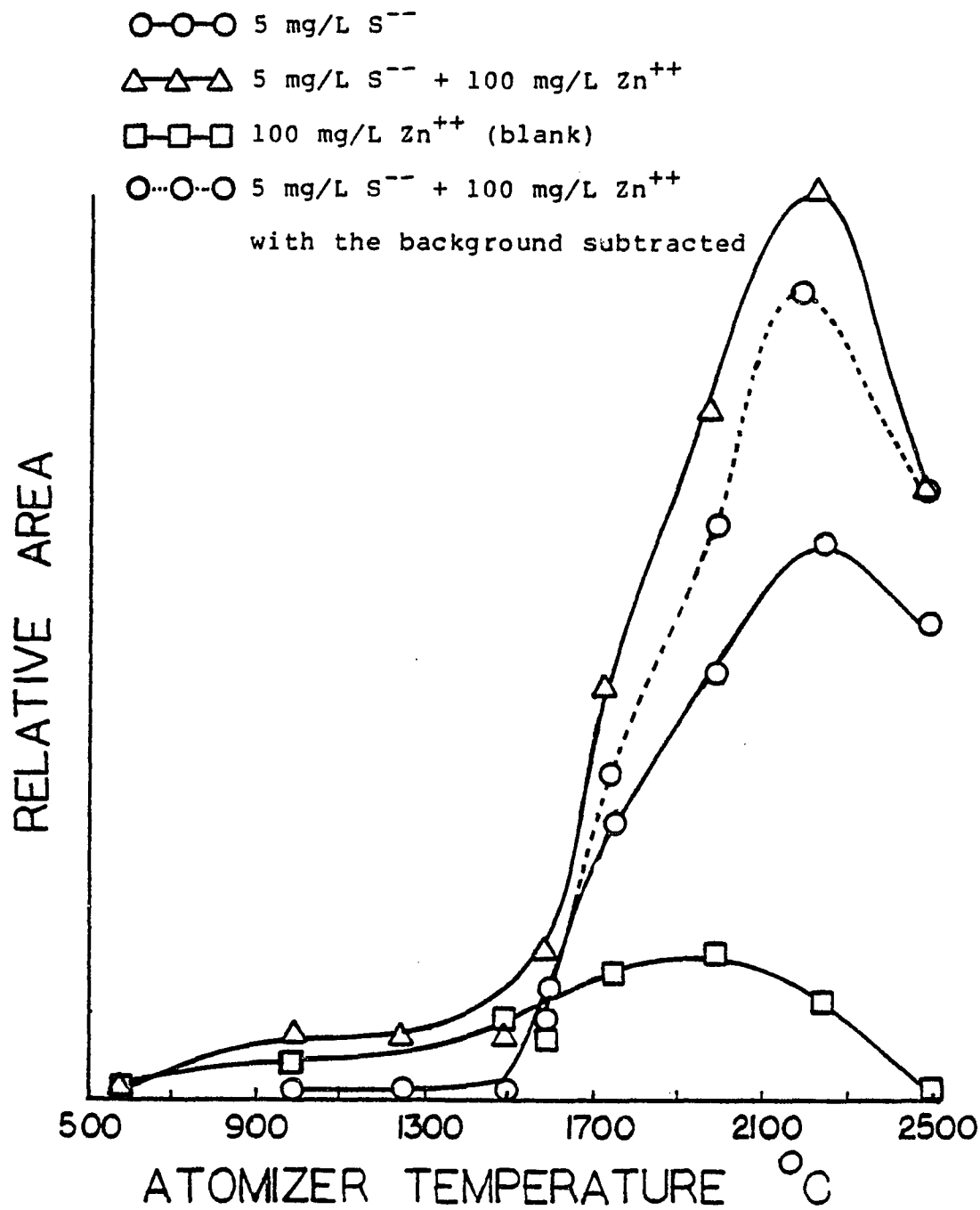


in the presence of calcium ion is not understood. Despite its existence the appearance temperature appears to be 2300°C.

In the case of sulfide in figure 22, the appearance temperatures for sulfide by itself and in the presence of 100 mg/L zinc ion are the same. Apparently the zinc ion has no effect on the vaporization of sulfide, even though at a temperature of 1750°C and higher, the signal is enhanced by the presence of zinc ion. However, the existence of the zinc ion enhancement may indicate there was some type of interaction with the sulfide ion. Possibly there was no zinc-sulfide-ion interaction, but if zinc vapor managed to get into the flame, then there may have been a chemiluminescent reaction taking place such as that observed for the element copper. This may have accounted for the large background signal from the blank solution. In section III it was shown that calcium ions did not get to the burner. However, zinc is more volatile than calcium, because zinc was used as the chloride salt (b.p. 732°C). Therefore, it is possible that zinc chloride may reach the burner.

From absorption spectroscopy, Yasuda and Kakiyama (100) showed that when metal sulfates were reduced in an atomizer they formed the metal plus sulfur dioxide. Thermodynamic calculations (101) show also that the following reaction is spontaneous when magnesium sulfate is heated over 1100°C

Figure 22: Peak area as a function of the atomizer temperature. Sulfur is in the form of sodium sulfide, and zinc is in the form of zinc nitrate.



in a graphite atomizer.

$$2C + MgSO_4 \longrightarrow SO_2 + 2CO + Mg$$

Presumably, other metal sulfate reactions, such as the reaction involving sodium sulfate, are thermodynamically favorable at 2500°C as well. In most cases, reduction takes place in a graphite atomizer. Therefore, one might expect the appearance temperature to be dependent on the relative ease at which a particular sulfur compound is reduced. One would therefore expect the above reduction to take place fairly easily, where the conversion of sulfide to sulfur dioxide is unlikely to occur, since this is an oxidation reaction. Since oxidation reactions are not favored in the atomizer, then it is very possible that the atomizer must reach a higher temperature in order for the sulfide to undergo some type of "oxidation" reaction. Apparently this reasoning is not correct because the appearance temperature for sulfide is 200°C less than that of the sulfate.

One may suggest that sulfide might be oxidized to S_2 instead of SO_2, especially since there would be no oxygen available in the atomizer. But, thermodynamic calculations show that the following reaction is not spontaneous at a temperature of 2300°C (data was not available at higher temperatures).

$$2MgS + 4C \longrightarrow S_2 + 2MgC_2$$

Of course other metal sulfide reductions may be favorable at this temperature, however no data was available on these. In general it is difficult to predict various mechanisms since the atomic absorption literature is fairly vague on the subject. Most workers are more concerned about the reduction of metal ions as opposed to the reduction mechanisms involving the anion present.

Figure 21 also shows that the peak height generally follows the same trend as peak area. The precision for peak height is not as good. One reason for this is related to the fact that samples with pure sulfate were randomly interspersed with those containing sulfate and calcium ion. After a sample containing calcium ion was fired in the atomizer, there was apparently a trace of calcium salt left. This trace of calcium apparently was not swept out with the two-second-high-temperature firings that were run between samples. As a result, the integral was not affected much, but the peak was shorter and broader. This caused poor precision for peak height measurements.

Interferences

Table 3 shows the extent of interference of various ions on both the sulfate and sulfide signal. The first column shows the magnitude of the signal caused by the metal ion itself. The reason the metal gives a signal is not understood.

However, it is possible that a molecular compound is formed in the atomizer which is carried over to the burner where it is excited, causing an emission of light. If this is the case, an interference filter could possibly eliminate it. The instrument is not sensitive enough to measure the contamination of sulfur in the metal salts used, especially since ACS reagent grade chemicals were used. The metal background signal was subtracted from each sulfur sample. In the case of the iron III ion the large signal obtained is probably caused by the nitric acid used to prevent hydrolysis. Figure 23 shows that a signal does arise from nitric acid alone and also in the presence of iron III. Possibly nitrogen in this form gives rise to cyanogen, which may emit light when carried over into the burner.

In some cases the enhanced signal from the sulfur compound, plus the metal ion is greater than that of the signal from the sulfur and metal ion alone. Obviously this would indicate there is some type of interaction between the metal and sulfur compound. In other cases, the presence of

Table 3

Summary of Metal Ion Interferences for Sulfur

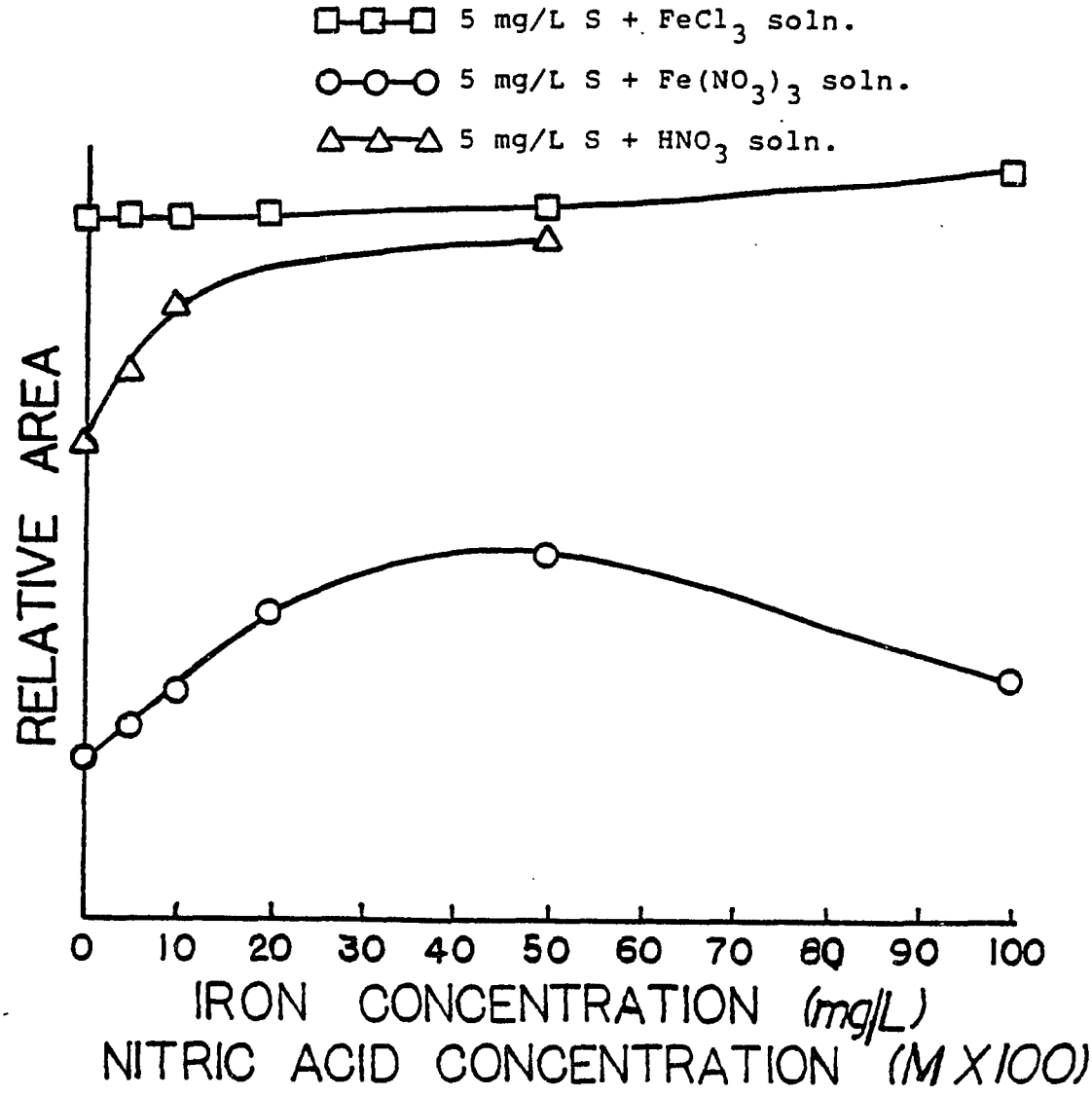
The data shown in the body of the table, in the first 3 columns, represent the percentage of the integral from a solution of 5 mg/L sulfur as sulfate. Data in the 4th and 5th columns, represent percentages from a solution of 5 mg/L sulfur as sulfide.

	Percent of peak area for 5 mg/L S (as sulfate)			Percent of peak area for 5 mg/L S (as sulfide)	
Ion	10 mg/L ion Blank	5 mg/L S + 10 mg/L ion	5 mg/L S + 100 mg/L ion	5 mg/L S + 10 mg/L ion	5 mg/L S + 100 mg/L ion
Al III	32%	75%	70%	33%	82%
Zn II	14	111	76	250[b]	197[b]
Cr III	11	66	60	28	18
Ni II	21	85	51	187[b]	135[b]
Cu II	55	100	109	246[b]	156[b]
K	38	91	174	115	197
Mg	38	81	51	59	46
Ca	79	92	79	--	--
Fe III[a]	132	92	132	64[b]	159[b]
Bromide	28	128	119	82	85
Iodide	49	104	98	--	--
Arsenate	77	85	132	--	--

[a]In 0.1 M nitric acid

[b]Formed a colloidal suspension

Figure 23: Sulfur signal as a function of added iron III chloride, iron III nitrate, and nitric acid. A 5 mg/L sulfur solution was used. Sulfur is in the form of sodium sulfate. Atomization temperature 2500°C. The relative position of each curve is unrelated to the other two, since each curve is an average of data taken on separate tubes and days.



the metal caused a decrease in the sulfur signal. This behavior leads one to believe there is more than one type of mechanism giving rise to metal ion interferences.

Certain sulfide samples that were run are marked with an asterisk. This designates that a colloidal dispersion occurred when the metal ion and sulfide were mixed. Since these dispersions did not settle out (at least for several days), a sample could still be put into the atomizer. It is interesting to note that particles of a solid metal sulfide gave rise to a very large enhancement.

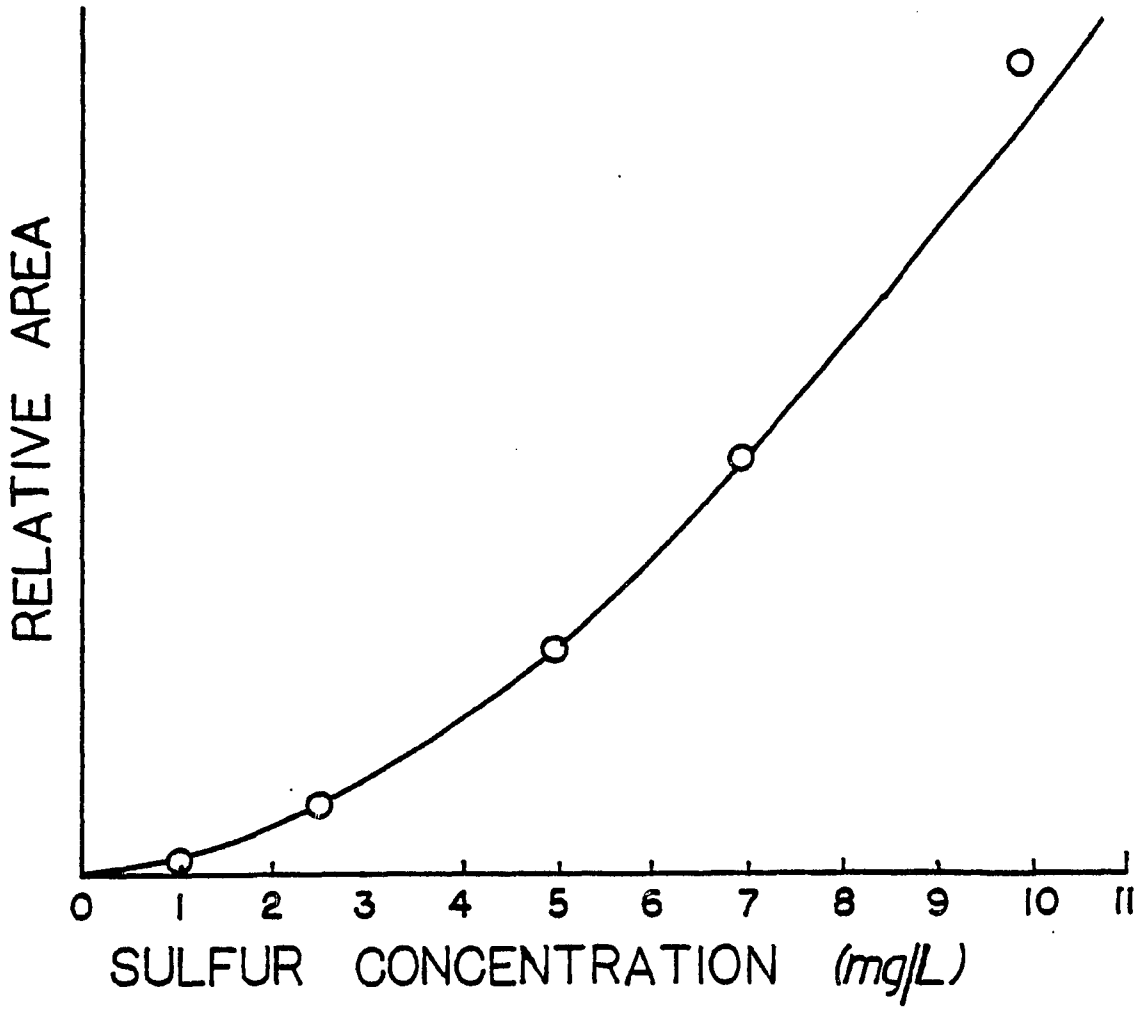
In addition to table 3, the interferences resulting from iron III and calcium were studied in greater depth. Figure 23 shows the signal for sulfate as a function of added iron. To prevent the formation of iron III hydroxide, the iron III salt must be acidified. When acidified with hydrochloric acid the signal is constant. However, when acidified with nitric acid, the signal reaches a maximum value, then decreases as shown in figure 23. When nitric acid alone is mixed with the sulfate to serve as a blank, it increases in a similiar manner as the iron III nitrate solution. The additional nitric acid required to keep the iron III ion in solution, is probably what is causing the signal to increase. A similiar graph was plotted for added calcium ion, the sulfur signal remained constant throughout the 100 mg/L calcium ion concentration range. The graph presumably showed no interference because no acid was added

in order to keep it in solution. Apparently it is the anion that causes the enhancement and not the hydrogen ion, because an experiment was performed where the sulfate signal was measured as a function of added hydrochloric acid and sodium chloride. In both cases the signal was constant showing no interference from either hydrochloric acid or sodium chloride at moderately low concentrations (i.e. less than 100 mg/L of chloride ion). When the concentration of chloride ion from sodium chloride approached 500 mg/L, the sulfur signal increased 33%. When the concentration of chloride from hydrochloric acid approached 500 mg/L, the sulfur signal decreased 31%.

Response of the Flame Photometer

Figure 24 shows a calibration curve for sulfur. At sulfur concentrations below about 5 mg/L the graph is nonlinear. This curve resembles the raw data used in the calibration curve shown in the article by Eckhardt et al (65). Both Eckhardt's work and this research used an analogous electronic device, to make the calibration curves linear. According to these workers, the slope of the calibration curve, x, will vary according to the type of sulfur specie entering the flame, and also the hydrogen and air flow rates. A value of x=1.95 for sulfur dioxide was used in this work, and Eckhardt's work, because this value

Figure 24: Calibration curve performed for sulfur. Sulfur is in the form of sodium sulfate. Atomization temperature 2500°C.



is for sulfur dioxide. This value was chosen because sulfur dioxide is believed to be the specie formed in the atomizer. Because this calibration curve is still not linear, it must indicate the hydrogen and air flow rates in our instrument were not optimized. This problem could be corrected by optimizing the flow rates of the gases.

One has confidence in the fact that the multifunction converter was working. Once it was assembled in the square root mode, the proper output voltage was obtained for each of nine different input voltages, between 1 and 10 volts. The device whose accuracy is 0.07% according to Burr-Brown, has proved to be accurate in all cases to at least 3% or better (the voltmeter used, limited the overall accuracy of the voltage measurements).

If one could extrapolate the curve from figure 24 to zero signal level, the detection limit is about 0.1 mg/L sulfur for a 25 μL sample. The relative standard deviation for eight, 5 mg/L sulfur samples run in a row is about 11%. This figure is probably high (normal precision is about 8%), but the precision for sulfur is generally not as good as it is for phosphorus, especially near the end of the useful life of the tube. The tubes were not permeated with silica and hence did not last as long, generally 100-120 atomizer firings. The sensitivity also varied with the tube's age, reaching a maximum (often doubled) in the middle of the tube's life. This same behavior was observed during

phosphorus analysis in a nonsilica-treated tube. The use of a silica-treated tube in a phosphorus analysis caused less of a sensitivity change during the tube's life. Possibly this same advantage of using a silica-treated tube would work for sulfur as well.

Conclusions

This section has given us a general idea of the behavior of sulfur compounds in the atomizer. However one is still lacking an understanding of the chemistry taking place in the atomizer. This is obvious from the speculations about the various appearance temperatures. Also there is little literature on the reactions taking place in the atomizer for various anions. For example the explanations for predicting various appearance temperatures seems to be incorrect. Since a metal sulfate is a weaker ionic bond than that of a metal phosphate, one expected the appearance temperature for sulfate in the presence of calcium to be much lower than that of phosphate in the presence of calcium. In fact one thought the calcium would not interfere at all. But instead, the appearance temperature for sulfate in the presence of calcium was only at about 1400^{o}C. This 900^{o}C difference in temperature was unexplainable according to one's understanding of the reactions involved.

Probably the most well studied phenomenon; was the effect of interfering metal ions on the sulfur signal. Table 3 gives a general idea as to the extent of interference on sulfate and sulfide. Figure 23 shows a more detailed study on the effect of iron III ion and nitric acid. Figures 21 and 22 also give information on the extent of interference as a function of atomizer temperature. All the previous work done on interferences was done at 2500°C. The relative degree of interference for calcium and zinc ions on their respective sulfur signals in figures 21 and 22 does not agree with those found in table 3. The trend is the same, but the percents of sulfur peak calculated from the graphs at 2500°C do not agree with those calculated in table 3 because these three studies were done on three different tubes. Apparently either each tube affects the extent of interference to a different degree, or the fact that the experiments were done at different times may be the cause of the disagreement.

So far the extent of interference for a number of elements has been established at various concentration levels. However, one does not understand the mechanism of the interference or how it can be prevented. Before this method of sulfur analysis is developed into an analytical technique, more work should be performed in two major areas.

One area is the calibration curve should be further investigated since it is nonlinear. A means should be sought to optimize the flow rates of the gases and to also keep them more constant.

The interference problem should also be solved. But to solve this problem one must also gain a better understanding of the atomizer chemistry. A better understanding would possibly allow one to predict what changes need to be made in either the atomizer design or chemistry that would eliminate the metal ion interference.

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